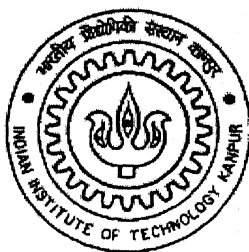# TEMPERATURE DEPENDENCE OF SELF DIFFUSION IN LIQUID METALS

A Thesis submitted
in partial fulfilment of the requirements
for the Degree of

Master of Technology

by

CHOWDAM JAYARAM

to the

Department of Chemical Engineering

INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

January 2001

CERTIFICATE

It is certified that the work contained in the thesis entitled **TEMPERATURE DEPEDENCE OF SELF-DIFFUSION IN LIQUID METALS,** by **CHOWDAM JAYARAM (Roll number 9910209),** has been carried out under our supervision and that this work has not been submitted elsewhere for a degree.

Dr. R.Ravi

Associate professor

Department of Chemical Engineering

Indian Institute of Technology

Kanpur-208016.

Dr. R.P Chhabra

Professor and Head

Department of Chemical Engineering

Indian Institute of Technology

Kanpur-208016.

January 2001.

ACKNOWLEDGEMENT

I express my deepest sense of gratitude to my thesis supervisors Dr. R.P.Chhabra and Dr. R. Ravi for their excellent guidance, encouragement, criticisms and advices made during this work.

I would like to express my sincere thanks to my friends, Madhav Krishna, Anil Kumar, Prabhakar, Bheema Rao, Narasimha Rao, Swain and Prasad for making my stay at I.I.T Kanpur a memorable one.

My special thanks to the faculties and authorities of I.I.T Kanpur who makes this institution an excellent learning place.

Chowdam Jayaram

ABSTRACT

A temperature dependent hard sphere diameter is found from viscosity data for sixteen liquid metals. This diameter is used to calculate self-diffusion coefficients using the corrected Enskog equation and Stokes- Einstein expression. While both these models underpredict the value of the molecular diffusivity, the accuracy of prediction is comparable to that obtained using the Protopapas-Parlee hard sphere diameter that is obtained from the diffusivity data itself. This scheme is proposed herein has a distinct advantage because viscosity data is available for many more systems than the diffusion data. The universal applicability of corresponding states model has also been tested using various potential parameters; However, the findings are somewhat inconclusive at least at this stage.

Dedicated

To

My parents

CONTENTS

List of Tables

List of Figures

NOMENCLATURE

Capital Letters

A (Chapter2)	A constant or a parameter
A (Chapter 3)	Amplitude, eV
B	A parameter
C	A parameter or a constant
$C_{AW}(\eta)$	Correction factor
$f(\eta^*)$ (Chapter 3)	Correction factor for Enskog equation
C_μ	Correction factor for Enskog viscosity equation
D	Self-diffusivity, m^2/s
D_o	A constant
D^*	Reduced diffusion coefficient
$G(T^*)$	Function of potential energy and pair distribution function
H_D	apparent activation energy for diffusion, $kcal/mol$
H_μ	apparent activation energy for viscous flow, $kcal/mol$
K_F	Fermi wave number
K	Thomas-Fermi screening constant
M	Atomic weight
N	Avagadro's number, 6.023×10^{23} $atoms/mol$
R	Gas constant, 8.314 $J/mol\ K$
R	Radius, m
T	Absolute temperature, K
T^*	Reduced temperature
V	Atomic volume, $m^3/g\text{-}atom$

V^*	Reduced volume
Z	Compressibility factor
Z	Effective valency
Z_s	Number of s-electrons
Z_d	Number of d-electrons

Small letters

a	Van der waals constant
a_o	Bohr's atomic radius, m
$g(r)$	Pair distribution function
k	Boltzmann's constant, 1.38066×10^{-23} J/K
m	Atomic mass, kg
m (chapter 3)	Lennard-Jones adjustable parameter
n	Number density
n (chapter 3)	Lennard-Jones adjustable parameter
p	pressure of the hard sphere fluid, Pa
r_o	Equilibrium nearest distance, m

Greek Symbols

α	An attenuation factor
β	Phase
δ	Distance parameter, m
ε	Energy parameter, eV
$\phi(r)$	Potential energy function, eV
η	Packing fraction
μ	Viscosity, $pa\text{-}s$
π	A constant, 3.147
ρ	Density, kg/m^3
σ	Hard sphere diameter, m

υ	Specific volume, kg/m^3
ξ	Friction coefficient

Subscripts

m	At melting point
E	Enskog
S-E	Stokes-Einstein

Superscripts

*	Reduced quantity

Chapter 1

INTRODUCTION

1.1 Introduction

The study of transport coefficients of liquid metals is important for various scientific and engineering reasons. A correct theoretical interpretation of their values would allow us to draw conclusions about the nature of ionic and electronic motions and interparticle interactions in such liquids. Also, a method of estimating their values would be of great use in the design of chemical, metallurgical and other industrial processes involving mass transfer by diffusion.

The process of diffusion is defined as the transport of mass from one region to another on an atomic scale. Diffusivity values in liquid state are much higher than those in the solid state. In the case of molten metals, diffusivities in the two states differ by a factor of 100 to 1000. The high atomic mobility of most metals just above their melting temperatures, wherein diffusivities of the order of 10^{-9} m^2/s, is one of the most characteristic properties of liquids.

The knowledge of self and binary diffusion coefficients in liquid metals is important for rational prediction of mass transfer rates in a number of existing and potential applications including the pyrometallurgical reprocessing of spent fuels from nuclear reactions, and in the production of metallic alloys in liquid phase. Several other processes such as corrosion, phase separation, crystal growth, etc., are governed by the rates of mass transfer, which, in turn, are primarily dependent on the value of the relevant diffusion coefficient. Experimental values of diffusion coefficients are used whenever available. Such data are, however, limited because of the difficulties inherent in the experimental determination of diffusivity especially at elevated temperatures.

Furthermore, it is unlikely that experimental values will ever become available for all systems of practical interest and/or at all values of temperature. It is thus often necessary to either predict the missing values or to extrapolate the existing values of diffusion coefficients; hence the need for a sound theoretical framework for predicting self-diffusion coefficients in molten metals is obvious. More reliable and accurate experimental data for self-diffusivities of various liquid metals are therefore needed so as to test and develop theories.

Different techniques have been developed for the measurement of diffusion coefficients of liquid metals system but theoretical studies have so far been limited to those involving a few liquid model approaches. Three distinct theoretical approaches have been used in the past to predict the values of self-diffusion coefficients of liquids. They are 1) the study of particular models for the liquid state combined with proposed mechanism for self diffusion, 2) the application of corresponding states principles, and 3) the use of molecular dynamics calculations.

The most familiar and notable example of the first approach is the Stokes-Einstein relationship between the self-diffusion and viscosity coefficients of a fluid. It is derived by assuming that the molecular fluid surrounding a diffusing particle can be described as a continuous fluid satisfying the usual hydrodynamics equations. Another example is the jump diffusion model; in this approach, the mechanism of motion is the jump of single atom or molecule from one equilibrium position over an activation energy barrier into a neighboring vacant site (hole) in the liquid.

The second basic approach for the liquid state is hard sphere theory. Hard sphere models have long been used to estimate self-diffusion coefficients of liquids in general and liquid metals in particular (Ascarelli and Paskin, 1967; Vadovic and Colver, 1970). The main reason for this is that the hard sphere model is a good approximation at least for the prediction of liquid properties. Further, analytical expressions are available for the diffusion coefficient (as well as for other transport properties) of hard spheres. These

expressions require, apart from the temperature and density, only one parameter, namely the effective hard sphere diameter. Often the hard sphere diameter is used as an adjustable parameter chosen so as to fit the predictions of the theory to available experimental data on diffusion. Clearly, the predictive capability of such an approach is very limited.

Studies involving a *priori* determination of hard sphere diameters for transport property calculations have been relatively few. Ben-Amotz and coworkers (Ben-Amotz and Herschbach, 1990; Ben-Amotz and Wills, 1993) proposed a scheme for determining hard sphere diameter from liquid compressibility data. Using this diameter in conjunction with Enskog theory, translational and rotational diffusion coefficients in n-hexane were predicted with reasonable success. However, given that Enskog theory itself is inadequate for hard spheres at higher densities, the need for a most sound theoretical basis is obvious. The Enskog theory is based on the assumption that an atom undergoes a series of hard-core binary collisions with its neighbors and that successive binary collisions are uncorrelated with each other. This approach has been used by Dymond and Alder (1966) to develop a theory of diffusion in Van der Waals fluid and by Ascarelli and Paskin (1968) to develop a theory for liquid metals. Many other examples of this type of approach could be cited, such as the fluctuation theory of Swalin (1959), the free volume theory of Cohen and Turnbull (1959) and the significant structure theory of Eyring and coworkers (Erying et al., 1964; Breitling and Erying, 1972).

For Lennard-Jones fluids, use of perturbation theory methods to estimate effective hare sphere diameters appears adequate for the prediction of diffusion coefficients (Ruckenstein and Liu, 1997). In the case of liquid metals, however, a similar approach was not quite as successful (Chauhan et al., 2000). This could be attributed to the long-range nature and softer core of the effective potentials of liquid metals. A further difficulty with the above approach is its reliance on accurate potentials, which may not be readily available.

3

Each of these theories makes implicit or explicit assumptions about the structure of a liquid and the nature of diffusive motion. The validity of such a theory must be judged partly on the basis of the correctness of its physical assumptions. Agreement between theoretical and experimental results is not sufficient to validate a theory, especially when it contains one or more disposable parameters. In fact, several of the theories mentioned above have proven to be fairly successful in the calculation of self-diffusion coefficients, despite the fact that they are based on completely different assumptions about the nature of transport process in liquids.

The necessity for making detailed assumptions about the liquid state is avoided in the second basic approach mentioned above, namely the use of the corresponding states principles. In this approach, the reduced self-diffusion coefficient for any liquid metal in any thermodynamic state is assumed to be a universal function of the reduced thermodynamic properties of that state. Pasternak and Olander (1967) have presented such a theory for self-diffusion in liquid metals, which builds upon the approach of Chapman (1966). Corresponding states methods are very useful for estimating transport coefficients, but they give little insight into the nature of liquids.

The third basic approach to the study of self-diffusion is the use of molecular dynamics (MD) calculations. In this approach, the atoms in a fluid are assumed to interact with each other by a certain type of inter-atomic potential. The Newton's equations for a finite number of such atoms are solved numerically, and the solution is used to calculate a wide variety of measurable properties, including the self-diffusion coefficient. A number of models (Verlet, 1967; Rahman 1964; Alder et al., 1970) have been investigated using this method. Molecular dynamics calculations provide a wealth of information about structure and atomic motions in liquids, but they are prohibitively expensive in terms of computing requirements, and hence, cannot be routinely applied to all fluids of interest. However, from the available results of such calculations, it is possible to draw several general conclusions, which are useful in developing a general theory of self-diffusion. These conclusions can be summarized as follows:

1) Dense liquids with realistic interatomic potentials have a structure, which is in many ways similar to that of hard sphere fluid.

2) The self-diffusion coefficients of realistic model liquids are not sensitive to the hardness or softness of the repulsive part of the potential, and are similar to those of the hard sphere fluid under similar conditions.

3) For the hard sphere fluid, the physical picture behind the Enskog theory is remarkably accurate over the entire range of fluid densities.

4) The self-diffusion coefficient for hard spheres is very nearly the same as the result of the Enskog theory.

Thus molecular dynamics calculations allow circumventing the problem common to most theories of liquids, namely the uncertainty about the validity of the basic concepts.

1.2 Scope of present work

In view of the above considerations, it seems worthwhile to pursue an approach that retains the simplicity afforded by the hard sphere model but one that neither uses the diffusion coefficient data nor depends on the availability of potentials. Instead, the hard sphere diameter is determined from the viscosity data, which is generally more accurate than the diffusion data. This approach was adopted for two reasons. One, viscosity data is available for a large number of liquid metals and hence if this procedure is proved successful, it would enhance our capability for calculating diffusion coefficients of liquid metals. Secondly, in an earlier work, use of the hard sphere diameter prescription of Protopapas and Parlee (1974) in the Stokes-Einstein equation led to a satisfactory prediction of diffusion coefficients. It would be interesting to see if the connection between diffusivity and viscosity, when established indirectly through the hard sphere model has any advantages over the Stokes-Einstein model.

On the other hand corresponding states model has also been tested with various types of potential parameters to obtain a universal curve for viscosity and self-diffusion coefficients using Helfand and Rice (1960) equations for corresponding states principle.

Chapter 2

LITERATURE REVIEW

In this chapter, we will review the literature connected with the theoretical and empirical calculations of self-diffusion coefficient in liquids in general and in molten metals in particular. It is convenient to classify the available models into the following four categories:

1. Hard Sphere models
2. Hydrodynamic models
3. Corresponding States Theory
4. Other models

Now, the salient features alongwith their relative merits and demerits are recapitulated in the ensuing sections.

2.1 Hard Sphere models

This model takes into account the finite size of the molecules but neglects attractive forces. Furthermore, molecules are thought to be made-up of hard spheres just like billiard balls. For hard sphere molecules, there are no forces between the molecules when their centers are separated by a distance larger than σ, the hard sphere diameter, but the forces of repulsion become infinitely large when they touch, at a separation equal to the hard sphere diameter σ.

The main feature of this class of hard sphere models is that all real fluids behave as hard sphere fluids in the high temperature limit. At high temperatures, the real fluid equation of state approaches the hard sphere equation of state, and it is no longer

necessary to use the experimental density values to get good results. The potential function of a hard sphere fluid is expressed by the following equations:

$$\phi(r) = 0 \qquad \text{for } r > \sigma \qquad (2.1a)$$

$$= \infty \qquad \text{for } r \leq \sigma \qquad (2.1b)$$

Different authors have proposed a range of models for the estimation of viscosity and diffusion coefficients based on hard sphere theory. However, we will discuss some models, which have been found to be most useful in predicting the values of viscosity and self-diffusion coefficient of liquid metals.

2.1.1 An equation based on hard-sphere theory

An expression for the shear viscosity of a dense fluid of non-attracting hard spheres due to Longuet-Higgins and Pople (1956) has been discussed by Faber (1972) and is expressed in terms of the packing fraction η:

$$\mu = 3.8 \times 10^{-8} \frac{(MT)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}} \eta^{\frac{4}{3}} \frac{\left(1-\frac{\eta}{2}\right)}{(1-\eta)^3} \qquad (2.2)$$

Similarly Faber (1972) has given an expression for self-diffusion coefficient of liquid metals:

$$D = 4.9 \times 10^{-10} \left(\frac{T}{M}\right)^{\frac{1}{2}} V^{\frac{1}{3}} \frac{(1-\eta)^3}{\eta^{\frac{5}{3}}\left(1-\frac{\eta}{2}\right)} \qquad (2.3)$$

where M is the atomic weight (kg/g-atom), V is the atomic volume (m^3/g-atom), η is the packing fraction, μ is the viscosity of the liquid metals (Pa-s) and D is the self-diffusion coefficient of the liquid metals (m^2/s).

Further, Faber (1972) has also calculated these properties at melting point by taking packing fraction η to be equal to 0.45. Then equations (2.1) and (2.2) lead to:

$$\mu_m = 1.6 \times 10^{-7} \frac{(MT_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}} \qquad (2.4)$$

$$D_m = 4.0 \times 10^{-10} \left(\frac{T_m}{M}\right)^{\frac{1}{2}} V_m^{\frac{1}{3}} \qquad (2.5)$$

where subscript 'm' represents melting point conditions.

Iida and Gutherie (1988) showed that Equation (2.3) underestimates the value of μ_m by a factor of the order of 0.3.

2.1.2 Enskog Hard Sphere model

1. Equation for viscosity

Based on the hard sphere theory, Enskog (Chapman and Cowling, 1970) derived an equation for viscosity. In this formulation, viscosity is expressed in terms of the packing fraction and pair distribution function at contact of hard spheres g (σ) as follows:

$$\mu = \left(\frac{1}{g(\sigma)} + 3.20\eta + 12.18\,\eta^2 g(\sigma)\right)\mu_o \qquad (2.6)$$

$$\text{and} \qquad \mu_o = \frac{5}{16\pi\sigma^2}(\pi m k T)^{\frac{1}{2}} \qquad (2.7)$$

where m is the atomic mass, k is the Boltzman's constant, σ is the hard sphere diameter and η is the packing fraction.

2. Enskog Equations for self-diffusivity

The Enskog theory (Chapman and Cowling, 1970) assumes that an atom undergoes a series of hard-core binary collisions with its neighbors, and that successive binary collisions are uncorrelated with each other. This approach simply relates the diffusion coefficient with pair distribution function, which in turn is related to an appropriate equation of state. This simple model has the advantage that exact calculation of transport

coefficients at a given temperature and density can be obtained with only one adjustable parameter namely, the hard sphere diameter. Though, the correct estimation of the hard sphere diameter and hence the pair distribution function of the hard spheres in contact is a difficult task which some times leads to the failure of the theory.

The self-diffusion coefficient can be computed using the Enskog theory as:

$$\frac{D}{D_o} = \frac{1}{g(\sigma)} \tag{2.8}$$

where D_o is given as,

$$D_o = \frac{3}{8n\sigma^2}\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}} \tag{2.9}$$

the packing fraction, η, is given by the following equation:

$$\eta = \frac{\pi}{6} n\sigma^3 \tag{2.10}$$

n is the number density and is given by: $n = \frac{\rho}{m}$ (2.11)

where ρ is the atomic mass density.

Equation (2.8) can now be rewritten as

$$D = \frac{r}{2(Z-1)}\left(\frac{\pi kT}{m}\right)^{\frac{1}{2}} \tag{2.12}$$

where r is the hard sphere radius = $\sigma/2$.

For a hard sphere fluid the radial distribution function, $g(\sigma)$ is related to the compressibility factor, Z, by the following equation:

$$Z = 1 + 4\eta\ g(\sigma) = \frac{p}{nkT} \tag{2.13}$$

where p is the pressure of the hard sphere fluid.

The compressibility factor, Z, can be calculated using the equation of state. Percus and Yevick (1958) have given an equation for the compressibility factor Z as follows:

$$Z = \frac{1 + \eta + \eta^2}{(1-\eta)^3}. \qquad (2.14)$$

Carnahan and Starling (1969) have given an equation of state, which is superior to any existing hard sphere equation of state including that of Percus and Yevick (1958), and is given by:

$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1-\eta)^3}. \qquad (2.15)$$

2.1.3 Vadovic and Colver approach

Ascarelli and Paskin (1967) calculated the values of self-diffusion coefficient for liquid metals by using equation (2.12) with a correction factor $0.73 \left(\dfrac{\eta_m}{\eta} \right)$. Vadovic and Colver (1970) recognized that at atmospheric conditions, the repulsive hard sphere pressure must be balanced approximately by the attractive Van der Waals pressure. They evaluated the Van der Waals constant (a) at melting point by using $a = \dfrac{Z_m k T_m}{n_m}$. Further, they calculated the values of diffusion coefficients for nine liquid metals at melting point using both equation (2.14) and (2.15) with the equation (2.12). In equation (2.12), they used a correction factor $0.73 \left(\dfrac{\eta_m}{\eta} \right)^{\frac{1}{2}}$ and the hard sphere radius $r = \left(\dfrac{3}{4} \dfrac{\eta_m M}{\pi \rho_{mn} N} \right)^{\frac{1}{3}}$. They concluded that the agreement of all calculated values with the melting point experimental data was remarkable, particularly as pointed out by Ascarelli and Paskin(1967), the error of the data is generally on the order of 10 percent. Further, they concluded that Carnahan and Starling equation of state yields the stronger temperature dependence than that stipulated by Ascarelli and Paskin (1967).

2.1.4 Protopapas and Parlee approach

Protopapas et al (1973) have presented a semi-empirical approach for the calculation of self-diffusion coefficient of liquid metals. The basic assumption is that the self-diffusion coefficient of a liquid metal is equal to that of an appropriate hard sphere fluid. The hard sphere diameter (Protopapas and Parlee, 1974) is dependent upon temperature, and they developed a method for estimating this temperature dependence by exploring the relationship between the diameter and the interatomic potential energy function of the liquid metal was presented. The scheme for calculating the hard sphere diameter developed by Protopapas et al (1973) is given by:

$$\sigma = 1.126\sigma_m \left[1 - 0.112 \left(\frac{T}{T_m} \right)^{\frac{1}{2}} \right] \qquad (2.16)$$

where σ_m is the value of σ at the melting point and is given by:

$$\sigma_m = \left\{ \frac{6(\eta_m)M}{\pi \rho_m N} \right\}^{\frac{1}{3}} = 1.41 \left\{ \frac{(M)}{\pi \rho_m N} \right\}^{\frac{1}{3}} \qquad (2.17)$$

In the above equation Protopapas et al (1973) have taken $\eta_m = 0.472$. On further simplification, Eq. (2.15) becomes as:

$$\sigma = 1.288 \left(\frac{M}{\rho_m} \right)^{\frac{1}{3}} \left[1 - 0.112 \left(\frac{T}{T_m} \right)^{\frac{1}{2}} \right] \qquad (2.18)$$

Protopapas et al (1973) have used Eq. (2.18) in the Enskog equation (2.8) and obtained an equation for self diffusion coefficient as:

$$D = \sigma C_{AW}(\eta) \left(\frac{\pi RT}{M} \right)^{\frac{1}{2}} \frac{(1-\eta)^3}{8\eta(2-\eta)} \qquad (2.19)$$

where $C_{AW}(\eta)$ is the correction factor. They computed self-diffusion coefficient at melting points and compared with the experimental values for a series of liquid metals. A good agreement with experimental results with an average difference about 2 % was reported.

Khanna et al (1993) have calculated the value of the self-diffusion coefficient of liquid alkali metals and its temperature dependence using the Enskog hard sphere model. In their study, they tested the suitability of the Enskog theory for self-diffusion coefficient for various systems of different range of densities. They found that the pair distribution function of the hard spheres in contact, $g(\sigma)$ depends upon the model and its parameters.

2.2 Hydrodynamic Model

2.2.1 Stokes-Einstein Equation

Stokes-Einstein equation is derived based on the assumption that the molecular fluid surrounding a diffusing particle can be described as a continuous fluid satisfying the hydrodynamic equations. Therefore for a single particle moving in a continuum or for a single heavy particle moving in a molecular medium of lighter particles, Brownian motion theory predicts that the diffusion coefficient is inversely proportional to the frictional coefficient (ξ)

$$D = \frac{kT}{\xi} \tag{2.20}$$

where ξ is the frictional coefficient.

Stokes derived an expression for the frictional coefficient ξ for the case of a spherical particle of radius R, moving in a continuum having a coefficient of shear viscosity μ as:

$$\xi = 6\pi\mu R \left(\frac{1 + \dfrac{2\mu}{\beta R}}{1 + \dfrac{3\mu}{\beta R}} \right) \tag{2.21}$$

where β is the 'coefficient of sliding friction' between the diffusing particle and its surrounding continuum. There are two possible limiting conditions, namely $\beta = \infty$ and $\beta = 0$.

a) $\beta = \infty$:

When the diffusing particle is large, compared with the particle of the medium, β equals to infinity, i.e. there is no slip between the moving sphere and the fluid in contact with it. For this no slip condition, the frictional coefficient becomes:

$$\xi = 6\pi\mu R \qquad\qquad (2.22)$$

b) $\beta = 0$:

When the radius of the diffusing particle approximately equal to that of the medium then β becomes zero and in this case the frictional coefficient becomes:

$$\xi = 4\pi\mu R . \qquad\qquad (2.23)$$

In the above two extreme cases equation (2.20) may be written as

$$D = \frac{kT}{6\pi\mu R} \qquad \text{when } \beta = \infty \qquad (2.24)$$

$$D = \frac{kT}{4\pi\mu R} \qquad \text{when } \beta = 0 \qquad (2.25)$$

From the above two equations, one can show that the quantity $\dfrac{D\mu}{T}$ should be constant, provided that the molecular diameter is independent of temperature. In general, Stokes-Einstein equation can be written as:

$$D = \frac{kT}{\alpha\pi\mu R} \qquad \text{where } 4 \le \alpha \le 6. \qquad (2.26)$$

Clearly, when considering the phenomenon of self-diffusion, intuitively it appears that $\alpha = 4$ would apply. In fact, sufficient evidence is now available in the literature illustrating the applicability of Eq. (2.26) to both self-diffusion and inter-diffusion coefficients in molecular non-polar substances provided a judicious choice is made of radius R. For a macroscopic solid sphere, there is no ambiguity in the assignment of particle radius, R. For a molecule or atom in the case of liquid metals; however, R must be interpreted as some average molecular radius. Thus for ordinary liquids, some investigators have used $R = \left(\dfrac{2}{n}\right)^{\frac{1}{3}}$, where n is the number density of the pure substance in liquid or solid state at low vapour pressure, while others have used the procedures

outlined by Edwards (1970) to evaluate R. in many cases, all these schemes yield values close to each other.

2.3 Corresponding states model

According to corresponding states principles, the reduced viscosity or diffusivity of similar substances in any thermodynamic state should be a universal function of the reduced thermodynamic properties of that state such as reduced temperature and pressure if the molecules are simple (monoatomic or spherical) and if the potential energy of interaction can be represented by a universal two parameter function of the type:

$$\phi(r) = \varepsilon f\left(\frac{r}{\delta}\right) \tag{2.27}$$

where ε and σ are the energy and distance coordinates of the function minimum. Chapman (1966) has obtained an equation for viscosity by using Born and Green (1947) theory which is written as:

$$\mu = \frac{A\pi\, n^2 \delta}{\sqrt{\dfrac{3kT}{m}}} \int_0^\infty r^3 \frac{d\phi(r)}{dr}[1 - g(r)]dr \tag{2.28}$$

where A is a constant and δ is the distance parameter.

Chapman (1966) postulated the reduced viscosity to be a function of the reduced temperature T^* and reduced volume V^*, defined as follows:

$$\mu^* = f\left(T^*, V^*\right) \tag{2.29}$$

14

$$\mu^* = \frac{\mu \delta^2 N}{(MRT)^{\frac{1}{2}}} \tag{2.30}$$

$$T^* = \frac{kT}{\varepsilon} \tag{2.31}$$

$$V^* = \frac{1}{n\delta^3} \tag{2.32}$$

The corresponding states principle is further applied on the assumption that $g(r)$ should be a universal function of $x = r/\delta$ and T^*; when this change of variable is executed, and when the reduced quantities are substituted in Eq. (2.28), the final form obtained as follows:

$$\mu^*(V^*)^2 = G(T^*) \tag{2.33}$$

where $G(T^*) = C \int x^3 \frac{d(\phi(x)/\varepsilon)}{dx} \big[1 - g(x, T^*)\big] dx$

where C is a constant.

Thus $\mu^*(V^*)^2$ is a universal function of T^*, and when plotted against $1/T^*$ should generate a universal curve for all liquid metals. This is in fact the case. In order to establish a corresponding state plot of the function $\mu^*(V^*)^2$ vs. T^*, Chapman (1966) assumed that all liquid metals obey the same function $\phi(r)$. He used Lennard–Jones potential parameters for Sodium and Potassium determined by Ling (1956) and experimental viscosity data, then plotted $\mu^*(V^*)^2$ vs. $1/T^*$, using Goldschmidt atomic diameter (Smithells, 1962) for δ. Then from this plot Chapman (1966) evaluated ε for the remaining liquid metals. Furthermore, with the obtained values of ε, a relationship between ε/k and melting point temperature T_m was obtained as:

$$\frac{\varepsilon}{k,} = 5.2T_m \tag{2.34}$$

The generalized plot for all liquid metals obtained by Chapman (1966) is shown in fig 2.
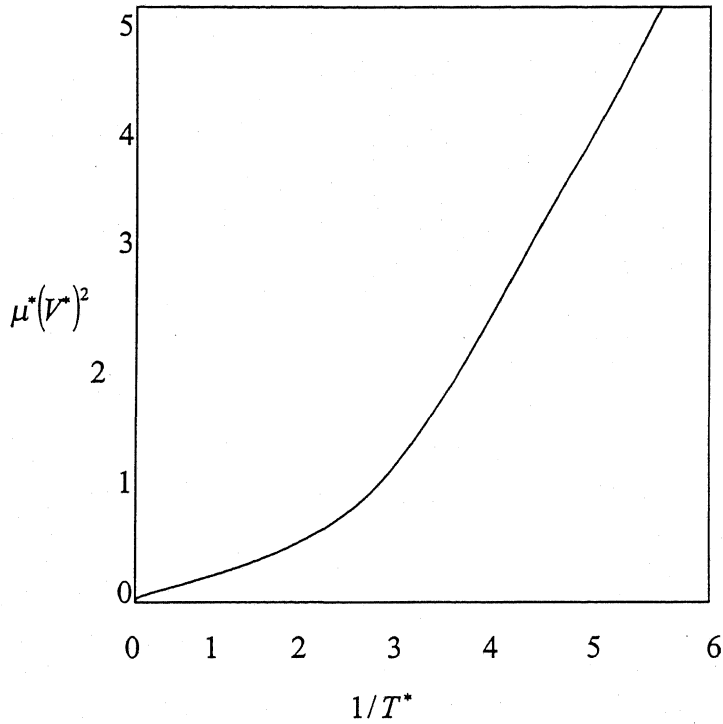
Fig 2 Reduced viscosities of liquid metals and their dependence on reduced temperature.

This universal curve is fitted into the following form:

$$\mu^*\left(V^*\right)^2 = \frac{0.3501}{\left(T^*\right)^{\frac{1}{2}}} \exp\left(\frac{0.3056}{T^*}\right) \tag{2.35}$$

Helfand and Rice (1960) have also shown that by assuming a pair potential $\phi(r) = \varepsilon \phi^*\left(\dfrac{r}{\delta}\right)$, where ε and δ are characteristic energy and distance parameters and ϕ^* is a universal function of r/δ. The reduced viscosity and the reduced diffusivity can be defined as:

$$\mu^* = \frac{\mu \delta^2}{(m\varepsilon)^{\frac{1}{2}}} \tag{2.36}$$

16

$$D^* = \frac{Dm^{\frac{1}{2}}}{\varepsilon^{\frac{1}{2}}\delta} \qquad (2.37)$$

Pasternak and Olander (1967) also correlated the self-diffusion coefficient and viscosity data using the corresponding states principles. The reduced viscosity and reduced diffusivity coefficient are defined as:

$$\mu^* = \frac{\mu}{\left(V^*\right)^{\frac{2}{3}}} \frac{\left(NV^2\right)^{\frac{1}{3}}}{\left(\dfrac{MR\varepsilon}{k}\right)^{\frac{1}{2}}} \qquad (2.38)$$

$$D^* = \frac{D\left(V^*N\right)^{\frac{1}{3}}M^{\frac{1}{2}}}{V^{\frac{1}{3}}\left(R\dfrac{\varepsilon}{k}\right)^{\frac{1}{2}}} \qquad (2.39)$$

where R is the universal gas constant.

Pasternak and Olander (1967) used the values of ε and Goldschmidt atomic diameter δ as obtained by Chapman (1966). He plotted $D^*/(V^*)^{1/3}$ vs. $1/T^*$ for ten liquid metals. All the data points were seen to lie on the same line with a spread of $\pm 20\%$.

2.4 Other models

2.4.1 Andrade Equation (Semi-theoretical)

Andrade (1934) regarded the atoms in the liquid state at the melting point as executing vibrations about equilibrium positions with random directions and periods just as in the solid state. Furthermore, assuming that the transfer of momentum of atomic vibrations from one layer to neighboring one produces viscosity of liquid and he gave the following equation for viscosity at the melting point.

$$\mu_m = 1. \times 10^{-4} \frac{(MT_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}}} \qquad (2.40)$$

This equation reproduces experimental data for liquid metals at their melting points with comparatively good accuracy. Furthermore, Andrade (1934) has presented an expression for temperature variation of viscosity.

$$\mu\upsilon^{\frac{1}{3}} = A \exp\left(\frac{c}{\upsilon T}\right) \qquad (2.41)$$

where υ is the specific volume and A and c are constants to be determined from experimental data. This equation has been found to fit experimental data with high degree of accuracy.

2.4.2 Empirical models

The temperature dependence of viscosity data in liquid metals can be approximate by an Arrhenius type relation and is given as:

$$\mu = A \exp\left(\frac{H_\mu}{RT}\right) \qquad (2.42)$$

where A and H_μ are constants.

Grosse (1961) has obtained the equation for the constant A using Andrade's formula for the melting point viscosity. This constant then becomes:

$$A = 5.7 \times 10^{-5} \frac{(MT_m)^{\frac{1}{2}}}{V_m^{\frac{2}{3}} \exp\left(\frac{H_\mu}{RT_m}\right)} \qquad (2.43)$$

Iida and Gutherie (1988) have reported expressions for H_μ, which relates rather well with the melting temperature T_m.

For normal metals: $(H_\mu)_n = 1.21\, T_m^{1.2}$ $\qquad$ (2.44a)

For semi-metals: $(H_\mu)_s = 0.75\, T_m^{1.2}$ $\qquad$ (2.44b)

Several investigators have presented empirical equations for self-diffusion in liquid metals. They have represented self-diffusion coefficient in the form of Arrhenius equation. One of such forms has been reported by Iida and Guthrie (1988) and is given by:

$$D = D_o exp\left(\frac{-H_D}{RT}\right) \qquad (2.45)$$

where H_D and D_o are constants. H_D is called the apparent activation energy and it can be evaluated by using the following equations:

For normal metals: $\left(H_D\right)_n = 2.5T_m^{1.5}$ \qquad (2.46a)

For semi-metals: $\left(H_D\right)_s = 2.00T_m^{1.5}$ \qquad (2.46b)

Larsson et al (1972) have reported that self-diffusivity in liquid metals at their melting point can be approximated as:

$$D_m = \frac{1}{6}\sqrt{\frac{3kT_m}{M}} \, V^{\frac{1}{3}}\beta \qquad (2.47)$$

The factor β is expected to be nearly constant for all liquid metals, approximately equals to 0.1. Iida and Guthrie (1988) have calculated the values of self-diffusion coefficient using this equation and compared with the experimental data. They concluded that this empirical equation reproduces the experimental data at melting temperature with good agreement.

Chapter 3

ANALYSIS AND VALIDATION

This chapter deals with the models, which have been used for the calculation of self-diffusion coefficients of liquid metals as a function of temperature.

3.1 Expression for viscosity

The Enskog hard sphere equation for viscosity is given by:

$$\mu_E = \left(\frac{1}{g(\sigma)} + 3.20\eta + 12.18\,\eta^2 g(\sigma) \right)\mu_o \tag{3.1}$$

where $\quad \mu_o = \dfrac{5}{16\pi\sigma^2}\,(\pi m k T)^{\frac{1}{2}} \tag{3.2}$

Molecular dynamics calculations have shown that Enskog's expression for a pure hard sphere fluid is not exact, since which do not take into account velocity correlations in the dense regime. A correction factor, due to Dymond (1976), as given by Castillo and Villaverde (1991) for shear viscosity as follows:

$$C_\mu = 1.02 + 10.61(n^* - 0.495)^3 + 247.49(n^* - 0.813)^3 \quad n^* > 0.813 \tag{3.3}$$

$$C_\mu = 1.02 + 10.61(n^* - 0.495)^3 \qquad\qquad 0.593 > n^* > 0.813 \tag{3.4}$$

$$C_\mu = 1.02 \qquad\qquad\qquad\qquad\qquad\quad 0.593 > n^* \tag{3.5}$$

where n^* is the reduced density and is given by $n\sigma^3$.

The corrected Enskog equation for viscosity is then, $\mu_{corr} = \mu_E C_\mu \tag{3.6}$

3.2 Equations for self-diffusion coefficient

We have calculated self-diffusion coefficient based on the corrected Enskog equation and also the Stokes-Einstein hydrodynamic model. In these calculations, we used the Protopapas and Parlee (1974) hard sphere diameter (PAP) and the diameters calculated from experimental viscosity data.

3.2.1 Enskog Equation

The Enskog expression for self-diffusion coefficient is given by:

$$\frac{D_E}{D_O} = \frac{1}{g(\sigma)} \tag{3.7}$$

where $D_o = \frac{3}{8n\sigma^2}\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}}$ $\tag{3.8}$

The final form of the Enskog equation is:

$$D_E = \frac{3}{8n\sigma^2 g(\sigma)}\left(\frac{kT}{\pi m}\right)^{\frac{1}{2}} \tag{3.9}$$

where ρ is the atomic density and is given by:

$$\rho = \rho_m + \Lambda(T - T_m) \tag{3.11}$$

where ρ_m and T_m are the density and temperature at melting point and Λ is a constant.

The pair distribution function, $g(\sigma)$ at contact is a function of packing fraction, and can be calculated from the compressibility factor, Z. The compressibility factor can be calculated from the Carnahan and Starling (1969) and Percus and Yevick (1958) equations of states. Since the equation of state due to Carnahan and Starling (CS) (1969) is more accurate than that of Percus and Yevick (1958), the CS equation of state will be used here. Therefore the pair distribution function at contact can be written g(σ) as:

$$g(\sigma) = \frac{Z-1}{4\eta} \tag{3.12}$$

where
$$Z = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \qquad (3.13)$$

The final form of the pair distribution function at contact, $g(\sigma)$ is:

$$g(\sigma) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \qquad (3.14)$$

Molecular dynamics simulations (Alder et al., 1970) on hard spheres have demonstrated the inadequacy of the Enskog results, especially at higher densities. In order to facilitate the analytical evaluation of diffusion coefficients, several expressions have been developed in which the 'corrected' value is expressed as:

$$D_E^{corr} = D_E f(n^*) \qquad (3.15)$$

In this work, we use an expression for $f(n^*)$ developed recently by Ruckenstein and Liu (1997) and is given by:

$$f(n^*) = 1 + 0.94605(n^*)^{1.5} + 1.4022(n^*)^3 - 5.6898(n^*)^5 + 2.6626(n^*)^7. \qquad (3.16)$$

3.2.2 Stokes – Einstein equation

When the radius of diffusing particle is approximately equal to that of the surrounding medium, the sliding friction coefficient β becomes zero and in this case the Stokes–Einstein equation becomes:

$$D_{S-E} = \frac{kT}{4\pi\mu R} \qquad (3.17)$$

In the above equation R is the radius of spherical particle moving in a continuum.

We have calculated self-diffusion coefficient using Protopapas and Parlee diameter (PAP) (1974) and with the diameters calculated from the experimental viscosity data.

3.3 Effective hard sphere diameter

The atomic diameter of elements is a parameter of fundamental importance for any consideration at the molecular level, dealing in particular with the models of hard spheres. The hard sphere diameter of a liquid metal, at a temperature T, understood to be the statistical minimum center to center distance of two atoms of metal during a two-body collision at temperature, when the metal atoms are assumed to be perfect spheres.

Many theories, models and approaches have been proposed for the evaluation of hard sphere diameters of liquid metals. Dymond and Alder (1966) have shown that the hard sphere diameter may be derived as a function of temperature from equilibrium data on the basis of the postulate that repulsive and attractive pressure terms in the Van der Waals equation of state counter balance each other. Ashcorft and Lekner (1966) have derived the temperature dependent hard sphere diameters. In their approach, the theoretical Percus-Yevick structure factor is fitted to the X-ray radial distribution function of the metal, and the packing fraction η of the best fit yields the hard sphere diameter at the temperature of the X- ray experiments.

A commonly used method is one based on the application of perturbation theory. Three distinct prescriptions are due to Barker and Henderson (BH) (1967), Weeks, Chandler and Anderson (WCA) (1972) and Lado (1984). All these approaches are based on splitting of the actual potential into a harshly repulsive reference potential and a weaker long-range perturbation. The three approaches differ in the nature of the splitting and also in their prescriptions for the effective hard sphere diameter and have been extensively applied to Lennard-Jones fluids with varying degree of success. All these three approaches have been discussed somewhere else (Chauhan et al., 2000).

A semi-empirical approach for derivation of the hard sphere diameters of liquid metals has been proposed by Protopapas et al (1973) assuming perfect collisions of atoms moving on parabolic potential wells. Their expression includes two constants, the values

of which were determined from experimental self-diffusivity data. The proposed equation for the hard sphere diameter is:

$$\sigma = 1.288 \left(\frac{M}{\rho_m} \right)^{\frac{1}{3}} \left[1 - 0.112 \left(\frac{T}{T_m} \right)^{\frac{1}{2}} \right] \qquad (3.19)$$

where M is the atomic weight and σ is in A° units.

We have calculated the hard sphere diameters from experimental viscosity data. In this approach, the corrected Enskog equation for viscosity (3.6) was used. The procedure for calculation of hard sphere diameters from experimental viscosity data is shown in detail in APPENDIX A. The values of diameter thus obtained are fitted to the form:

$$\sigma = A + BT + CT^2 \qquad (3.20)$$

where A, B and C are constants. In the above equation, σ is in A^o and T is in K.

Thus with the calculated diameter, we have calculated self-diffusion coefficients using the corrected Enskog equation (3.15) and Stokes-Einstein expression (3.17).

3.4 Corresponding states model

In this approach, an attempt has been made to test the universal applicability of corresponding states equations. Though there are many such approaches available in the literature, as discussed in chapter 2, we have chosen the one due to the Helfand and Rice (1960). According to their approach, the reduced properties can be expressed as:

$$\mu^* = \frac{\mu \delta^2}{\sqrt{m\varepsilon}} \qquad (3.21)$$

$$D^* = \frac{Dm^{\frac{1}{2}}}{\varepsilon^{\frac{1}{2}}\delta} \qquad (3.22)$$

$$T^* = \frac{kT}{\varepsilon} \qquad (3.23)$$

$$V^* = \frac{1}{n\delta^3} \qquad (3.24)$$

In the above equations ε and δ are energy and distance parameters respectively. In this case, ε becomes potential well depth, m is the mass of atom and the superscript '*' refers to reduced parameters.

3.4.1 Effective pair potentials

In order to calculate the potential depth parameter, ε and atomic distance, δ, we need effective pair potentials for liquid metals. The effective interparticle potential of liquid metals is widely modeled as exhibiting a short-range repulsion and long-range oscillations. Most of the potentials have been obtained from structure factor data. There are, however, several intrinsic difficulties associated with this procedure. First, since the structure factor data is relatively insensitive to the details of the potentials, one requires very accurate data to obtain an accurate potential. Such data is generally difficult to obtain for liquid metals. Furthermore, in much of the early work, these potentials have been obtained through route of integral equation theories that are only approximate at best and have in fact been since shown to be quite inaccurate.

Johnson et al (1964) (JHM) have shown that the inversion of experimental scattering data by means of the Born – Green (B-G) (1947) and Percus- Yevick (P-Y) (1958) integral equations yields a long-range oscillatory (LRO) pair potentials for a number of liquid metals. Their procedure (JHM) was to deduce the effective pair potentials from a knowledge of radial distribution function. The JHM long-range oscillatory potentials have the form:

$$\varphi(r) = A\left(\frac{r_o}{r}\right)^3 \cos(2k\{r + \beta\})\exp(-\alpha r) \qquad (3.25)$$

where A is the amplitude, r_o is the position of the first node, β is the phase, α is an attenuation factor and k is given by π/ wave length of oscillations.

Recent theoretical work (Hausleitner, 1988; Bari et al., 1991; Bari and Jorder, 1992) on liquid transition metals has used the effective pair potentials of Wills and Harrison (WH) (1983), which are based on a separate treatment of s-p and d states and, in addition, take in to account the effect of s-d hybridisation. According to Wills and Harrison (1983), the effective pair potential (EPP) is made up of an s-electron contribution, $\phi_s(r)$, a d-band contribution term, $\phi_b(r)$ and the repulsive contribution, $\phi_r(r)$ from the shift of d-band centre, given by:

$$\phi(r) = \phi_s(r) + \phi_b(r) + \phi_r(r) \tag{3.26}$$

The individual terms can be given by:

$$\phi_s(r) = Z_s^2 e^2 \cosh(Kr_c)\frac{e^{-kr}}{r} \tag{3.27}$$

$$\phi_r(r) = Z_d \frac{225}{\pi^2} \frac{h^2 r_d^6}{m_e r^8} \tag{3.28}$$

$$\phi_r(r) = -Z_d \left[1 - \frac{Z_d}{10}\right]\left(\frac{12}{n}\right)^{\frac{1}{2}}\left(\frac{28.1}{\pi}\right)\frac{h^2 r_d^3}{m_e r^5} \tag{3.29}$$

where Z_s is the number of s electrons, K is the Thomas-Fermi screening constant and is given by $K = \left(\frac{4K_F}{\pi a_o}\right)^{\frac{1}{2}}$ (3.30)

In the above equation K_F is the Fermi wave number and is given by

$$K_F = \left(\frac{9\pi Z_s}{4r_o^3}\right)^{\frac{1}{3}} \tag{3.31}$$

where r is the interatomic distance, r_o is the atomic radius, r_c is the pseudo potential core radius, r_d is the d-state radius, Z is the valency, Z_d is the number of d-electrons, n is the nearest neighbour co-ordination number, a_o is the Bohr atomic radius, m_e is the mass of electron and e charge of electron.

Z_d can be calculated by using the following equation:

$$Zs = Z - Z_d \tag{3.32}$$

Table 3.1 Liquid metals and their Potential parameters.

| Metal	Potential parameter		Potential type	Source
	ε (K)	σ (A°)		
Ag	3325.6	2.88	Lennard-Jones (m-n)	Zhen and Davies (1983)
Cd	1561	3.112	Lennard-Jones (m-n)	Zhen and Davies (1983)
Co	1108	2.78	Wills and Harrison	Wills and Harrison (1983)
Cs	603.65	5.2	Long-range oscillatory	Johnson et al (1964)
	406.1865	5.19	Lennard-Jones (6-12)	Sengupta et al (1977)
	385.5	4.76	Pseudo	Ranganathan and Pathak (1994)
Cu	3401.1	2.5	Lennard-Jones (m-n)	Zhen and Davies (1983)
Fe	1892	2.85	Wills and Harrison	Wills and Harrison (1983)
Hg	597.85	5.20	Long-range oscillatory	Johnson et al (1964)
K	712.7	4.54	Lennard-Jones (m-n)	Zhen and Davies (1983)
	493.37	4.51	Long-range oscillatory	Johnson et al (1964)
	421.4	4.11	Pseudo	Ranganathan and Pathak (1994)
	464.213	4.64	Lennard-Jones (6-12)	Sengupta et al (1977)
Li	713.6	3.00	Lennard-Jones (m-n)	Zhen and Davies (1983)
	447	3.21	Long-range oscillatory	Johnson et al (1964)
	567.1	2.73	Pseudo	Ranganathan and Pathak (1994)
	371.37	3.15	Lennard-Jones (6-12)	Sengupta et al (1977)
Na	798.9	3.66	Lennard-Jones (m-n)	Zhen and Davies (1983)
	516.6	3.25	Long-range oscillatory	Johnson et al (1964)
	421.4	4.12	Pseudo	Ranganathan and Pathak (1994)
	510.633	3.82	Lennard-Jones (6-12)	Sengupta et al (1977)
Ni	758.12	2.74	Wills and Harrison	Wills and Harrison (1983)
Pb	2215.9	3.48	Lennard-Jones (m-n)	Zhen and Davies (1983)
	1126	3.30	Long-range oscillatory	Johnson et al (1964)
Rb	610.7	4.85	Lennard-Jones (m-n)	Zhen and Davies (1983)
	377.3	5.05	Long-range oscillatory	Johnson et al (1964)
	402.2	4.41	Pseudo	Ranganathan and Pathak (1994)
	464.21	4.97	Lennard-Jones (6-12)	Sengupta et al (1977)
Tl	1759.5	3.41	Lennard-Jones (m-n)	Zhen and Davies (1983)
Zn	1681.5	2.76	Lennard-Jones (m-n)	Zhen and Davies (1983)
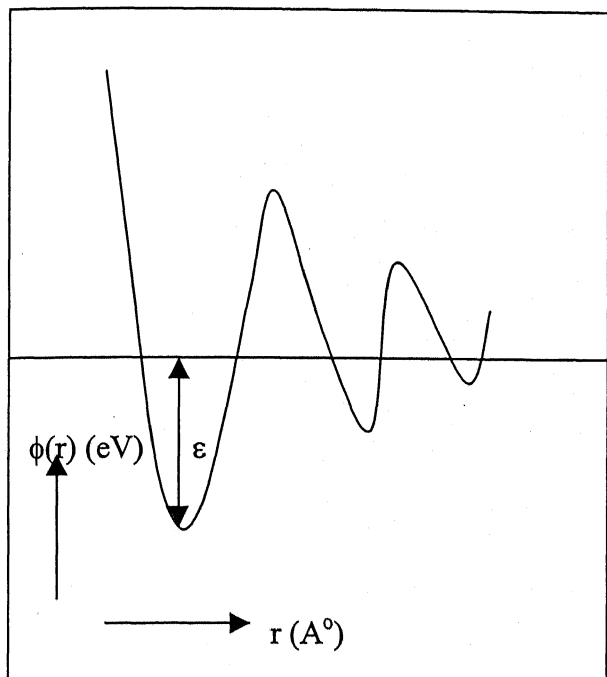
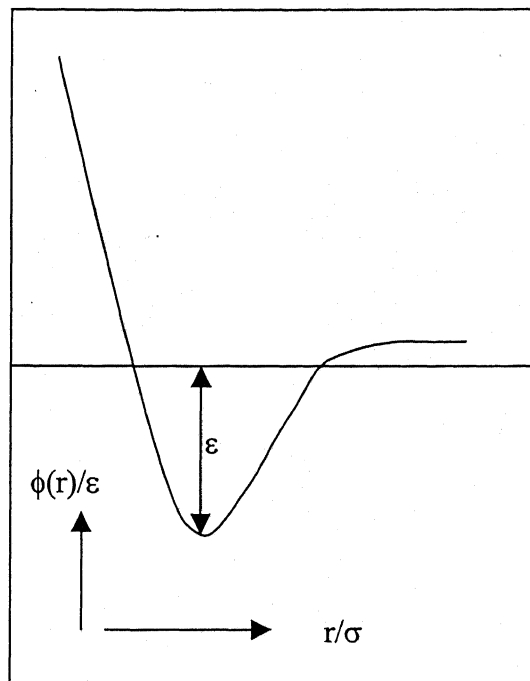Fig 3.1 Schematic representation of long-range oscillatory potentials (Johnson et al., 1964).

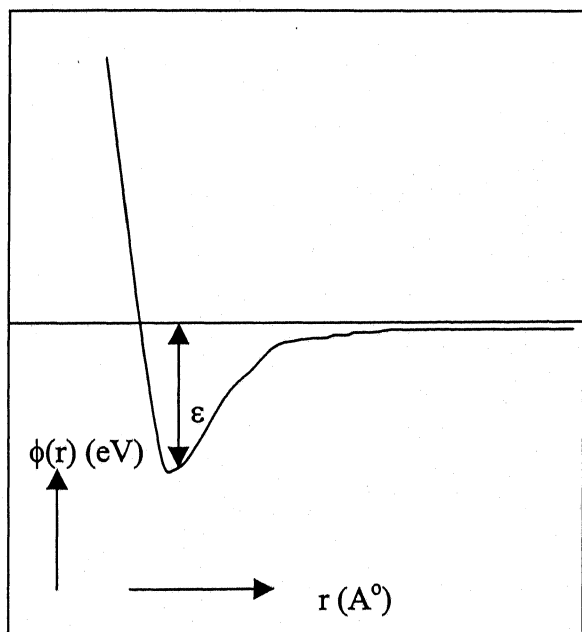Fig 3.2 Schematic representation of pseudo potentials (Ranganathan and Pathak, 1994).

Fig 3.3 Schematic representation of WH potentials (Wills and Harrison, 1983).
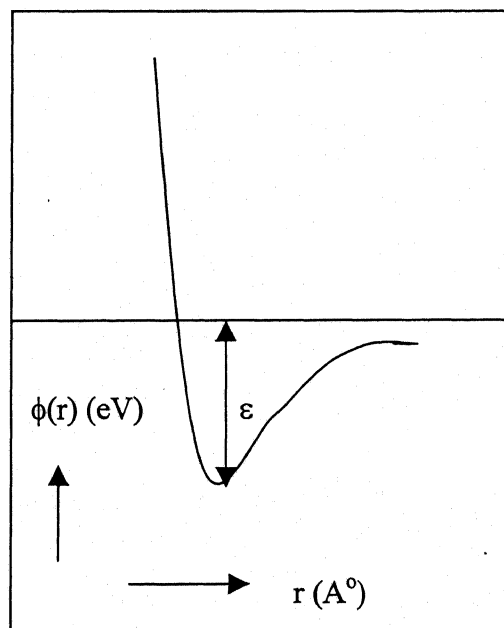

Fig 3.4 Schematic representation of Lennard-Jones potentials (Zhen and Davies, 1983).

Many workers have used inter-atomic potentials in the calculation of transport properties of liquid alkali metals. Sengupta et al (1977) have calculated self-diffusion coefficient of alkali metals using Lennard- Jones (L-J) potentials. They listed energy and distance parameters. Ranganathan and Pathak (1994) have used pseudo potentials of the form $\phi(r) = \varepsilon\phi\left(\dfrac{r}{\delta}\right)$ in the calculations of self-diffusion coefficients.

Zhen and Davies (1983) have developed a new approach to calculate the Lennard-Jones n-m potential energy parameters for metals using experimental cohesive energy data. They employed this approach because Lennard-Jones 12-6 potential is not a good representation of the potential for metals. One way to improve the agreement between the potential model and the experimental data is to use the generalized form of the interatomic potential (the Lennard-Jones n-m potentials),

$$\phi(r) = \varepsilon\left\{\frac{m}{n-m}\left(\frac{r_o}{r}\right)^n - \frac{n}{n-m}\left(\frac{r_o}{r}\right)^m\right\} \quad n > m, \tag{3.33}$$

where r_o is the equilibrium nearest distance between the atoms. This generalized potential has four adjustable parameters m, n, ε and r_o.

The schematic representations of these potentials are shown in the following figures (3.1- 3.4). The reduced viscosity and reduced diffusivity were calculated using these potential parameters and are listed in the Table 3.1. In the calculations of reduced viscosity and reduced diffusivity and their volume dependency, Pseudo potentials (Ranganathan and Pathak, 1993), Lennard-Jones (m-n) (Zhen and Davies, 1983) potentials were used. These results are presented and discussed in the next chapter.

Chapter 4

RESULTS AND DISCUSSION

4.1 Data accuracy

Reliable experimental values of both viscosity and self-diffusion coefficients encompassing varying temperature ranges were identified from the literature for sixteen liquid metals. It is also worthwhile to address the issue of the accuracy of such measurements. While experimental uncertainty varies from one technique to another and is strongly dependent on the purity of sample. It is generally believed that the available diffusion data are accurate to within 5-7% at best and about 20% at worst. Similarly, the accuracy of the viscosity data is also dependent on the technique and temperature but these are believed to be accurate to within 5% at best and about 10-12% at worst.

4.2 Hard sphere diameter

The hard sphere diameter,σ, was calculated using from the experimental viscosity data via the corrected Enskog expression. The list of sixteen metals, the sources containing viscosity data and the temperature range over which the data were used in the calculation of hard sphere diameters is shown the Table 4.1. The temperature dependence of hard sphere diameter, σ, was fitted to the form

$$\sigma(T) = A + BT + CT^2. \tag{4.1}$$

The parameters A, B and C were determined for each metal. The best values of these parameters along with their correlation coefficients are listed in the Table 4.2. Viscosity data for temperatures within +10% of the melting temperature were not considered for this purpose.

Table 4.1 Liquid metals and their sources for viscosity and diffusivity data

S.NO	Metal	T_m (K)	Viscosity	Temperature Range (K)	Diffusivity	Temperature Range (K)
1.	Ag	1233.65	Gebhart and Becker (1951)	1260-1400	Yang et al (1956)	1260-1400
2.	Bi	544.1	Yao and Kondic (1952)	560-680	Chauhan et al (2000)	540-680
3.	Cd	594	Miller (1952)	610-750	Chauhan et al (2000)	610-750
4.	Cs	301.65	Andrade and Dobbs (1952)	325-395	Chauhan et al (2000)	325-395
5.	Cu	1356	Landolt-Bornstein tables (1969)	1373-1573	Henderson and Yang (1961)	1370-1440
6.	Ga	303	Spells (1936)	330-365	Petit and Nachtrieb (1956)	330-365
7.	Hg	234.28	Innes (1956)	253-613	Hoffman (1952)	270-370
8.	In	429.55	Crawly and Thresh (1969)	440-619	Lodding (1956)	450-590
9.	K	336.75	Macleod (1938)	352-626	Rohlin and Lodding (1962)	350-490
10.	Li	452	Landolt-Bornstein tables (1969)	465-605	Murday and Cotts (1968)	465-605
11.	Na	371.05	Macleod (1938)	382-628	Meyer and Nachtrieb (1955)	390-500
12.	Pb	600.55	Landolt-Bornstein tables (1969)	612-955	Rothman and Hall (1956)	630-810
13.	Rb	311	Landolt-Bornstein tables (1969)	375-465	Norden and Lodding (1967)	375-465
14.	Sn	505	Walsdorfer (1983)	530-660	Careri et al (1958)	530-660
15.	Tl	576	Walsdorfer (1983)	590-640	Cahill and Grosse (1965)	525-640
16.	Zn	692.6	Yao and Kondic (1952)	720-860	Nachtrieb and Fraga (1963)	700-860

Table 4.2 Hard sphere diameter parameters calculated from experimental viscosity data

S. No	Metal	A (A°)	BX10^4 (A°/K)	CX10^8 (A°/K^2)	Correlation coefficient
1	Ag	2.7471	-1.5331	1.0478	0.999976
2	Bi	3.4504	-8.2745	2.9137	0.99999
3	Cd	2.8956	-2.4961	1.6283	0.999995
4	Cs	5.0116	-7.4249	-33.810	0.99999
5	Cu	2.0758	4.182	-20.164	0.999984
6	Ga	2.79	-7.316	33.262	0.999999
7	Hg	3.009	-11.1	73.418	0.9998
8	In	3.1111	-5.735	11.976	0.99974
9	K	4.4058	-9.8522	48.7957	0.99984
10	Li	2.8407	-3.2767	10.710	0.999991
11	Na	3.5624	-6.21	7.634	0.999898
12	Pb	3.2811	-4.0772	6.1966	0.999898
13	Rb	4.7368	-1.0957	27.306	0.999972
14	Sn	3.1292	-2.4508	-25.117	0.999995
15	Tl	3.2257	-4.496	4.2375	0.99998
16	Zn	2.65	-2.9242	11.19	0.99998

4.3 Diffusion coefficients

4.3.1 Hard sphere model

The hard sphere diameters calculated by the above method were used to obtain the self-diffusion coefficients using the corrected Enskog expression. Furthermore, self-diffusion coefficients were also calculated using the Protopapas and Parlee (1974) hard sphere diameters. The resulting values are compared with the experimental values and these are plotted in figures 4.1 to 4.16. The computed values of self-diffusion coefficients were also listed in the tables (4.3-4.18) along with their experimental values. The hard sphere model gives comparable predictions for most metals. The obtained values are within 20-25% of the experimental values which themselves may entail experimental uncertainty of the order of 20%. In Fig 4.1-4.16, solid line indicates the Corrected Enskog equation using the diameter calculated from experimental viscosity data, dash-dot-dash line indicates the corrected Enskog values using the Protopapas and Parlee diameter, broken line and dot line indicate the Stokes-Einstein equation using the diameter calculated form experimental viscosity data and Protopapas and Parlee diameters respectively and circle line indicates experimental diffusivity values.

The corrected Enskog hard sphere model underestimates the values of diffusion coefficients in most cases. In the case of Silver and Zinc, at low temperatures the Protopapas and Parlee diameter yields good values and as the temperature increases the extent of underestimation also increases. This model overestimates the values of diffusivities in the cases of Bi, In and Li. In the case of Bismuth, the Protopapas and Parlee diameter does very well compared to the other choices of diameter. In general all these models predict a weaker temperature dependence of the diffusivity than is observed experimentally.

Within the context of the hard sphere model, the Protopapas-Parlee diameter, except for Gallium, does not display any marked superiority over the diameters obtained from viscosity data. This is despite the fact that the Protopapas- Parlee diameters were obtained from a statistical analysis of diffusivity data (Protopapas et al 1973).

4.3.2 Stokes – Einstein Model

An examination of tables (4.3-4.18) or plots (4.1-4.16) reveals that in most cases, the predicted values are within 5-25% of the experimental values. From these tables, it is readily seen that this model consistently underpredicts the value of diffusion coefficient, though the extent of underprediction varies one metal to another and/or with temperature. Thus for Ag, K, Li and Pb the predictions become progressively worse as the temperature increases whereas in the case of In, the predictions become close to the experimental values. Yet in some other systems e.g. Sn and Rb, the divergence between the experimental and predicted values decreases as the temperature increases. Suffice it to say here that similar deviations have been widely reported in the literature even for ordinary liquids.

Some investigators have attributed these deviations to the non-spherical shape of diffusing molecule, and/or to solute-solvent interactions, etc., while numerous investigators have suggested ad hoc empirical modifications to improve the correspondence between the predictions of this model and experimental values of self-diffusion coefficient. Based on extensive data and heuristic considerations, many workers (Tyrrell, 1981; Pollack, 1981; Pollack and Enyeart, 1985) have argued that the self-diffusion coefficient depends upon the medium viscosity as:

$$D \propto \frac{1}{\mu^p},$$ (4.2)

where scores of values of p ranging from 0.53 to 0.69 have been documented in the literature and indeed Ziwanzig and Harisson (1985) have argued that there are no theoretical reasons to expect a single value of p to be universally applicable to all systems. Chauhan et al (2000) have attempted this modification in the study of liquid metals, and the values of p ranging from 0.62 to 1.56 were obtained, showing absolutely no correlation with any structural, molecular or thermodynamic quantity. This more or less reinforces the notation of Ziwanzig and Harisson (1985). It is worthwhile to point out here that such a wide variation in the value of p cannot be attributed to experimental uncertainty in the diffusion coefficient or viscosity. The only other way to improve the

Table 4.3 Self-diffusion coefficients and hard sphere diameters for liquid Ag

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \,(m^2/s)$		$D_{S-E} \times 10^9 \,(m^2/s)$		$D_{Expt} \times 10^9 \,(m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
1260	2.5706	2.5828	3.1093	2.7962	2.8872	2.8735	2.7214
1280	2.5680	2.5802	3.2127	2.8962	3.0270	3.0127	2.8574
1300	2.5655	2.5776	3.3176	2.9975	3.1648	3.1500	2.9901
1320	2.5630	2.5750	3.4240	3.1000	3.3054	3.2899	3.1275
1340	2.5605	2.5725	3.5318	3.2037	3.4486	3.4326	3.2668
1360	2.5580	2.5699	3.6411	3.3086	3.5944	3.5777	3.4080
1380	2.5555	2.5674	3.7518	3.4147	3.7428	3.7254	3.5509
1400	2.5530	2.5650	3.8638	3.5220	3.8937	3.8756	3.6950

Table 4.4 Self-diffusion coefficients and hard sphere diameters for liquid Bi

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \,(m^2/s)$		$D_{S-E} \times 10^9 \,(m^2/s)$		$D_{Expt} \times 10^9 \,(m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
540	3.0885	3.1466	2.2484	1.5239	2.0926	2.0539	0.8002
560	3.0784	3.1394	2.4347	1.6448	2.2915	2.2470	0.8700
580	3.0685	3.1322	2.6246	1.7687	2.4973	2.4465	0.9403
600	3.0588	3.1252	2.8178	1.8956	2.7094	2.6518	1.0111
620	3.0494	3.1184	3.0139	2.0254	2.9275	2.8627	1.0822
640	3.0402	3.1116	3.2123	2.1580	3.1517	3.0794	1.1533
660	3.0312	3.1049	3.4127	2.2933	3.3813	3.3011	1.2244
680	3.0225	3.0983	3.6147	2.4311	3.6166	3.5280	1.2953

Table 4.5 Self-diffusion coefficients and hard sphere diameters for liquid Cd

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \ (m^2/s)$		$D_{S-E} \times 10^9 \ (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
610	2.7494	2.7541	2.1294	2.0473	1.9676	1.9642	2.3595
630	2.7448	2.7484	2.2559	2.1916	2.1361	2.1333	2.5732
650	2.7402	2.7428	2.3858	2.3391	2.3096	2.3075	2.7913
670	2.7357	2.7372	2.5191	2.4899	2.4884	2.4870	3.0131
690	2.7311	2.7317	2.6557	2.6438	2.6719	2.6713	3.2383
710	2.7266	2.7263	2.7957	2.8007	2.8601	2.8603	3.4462
730	2.7221	2.7210	2.9389	2.9605	3.0527	3.0538	3.6963
750	2.7176	2.7158	3.0854	3.1231	3.2496	3.2518	3.9282

Table 4.6 Self-diffusion coefficients and hard sphere diameters for liquid Cs

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \ (m^2/s)$		$D_{S-E} \times 10^9 \ (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
325	4.7346	4.7398	2.6665	2.6045	2.5258	2.5230	2.6945
335	4.7249	4.7302	2.8520	2.7864	2.7488	2.7458	2.9364
345	4.7152	4.7208	3.0446	2.9727	2.9781	2.9746	3.1814
355	4.7054	4.7116	3.2443	3.1632	3.2157	3.2114	3.4370
365	4.6955	4.7025	3.4512	3.3577	3.4602	3.4552	3.6945
375	4.6856	4.6935	3.6651	3.5563	3.7131	3.7069	3.9559
385	4.6756	4.6846	3.8863	3.7586	3.9721	3.9645	4.2209
395	4.6656	4.6758	4.1145	3.9647	4.2386	4.2293	4.4888

Table 4.7 Self-diffusion coefficients and hard sphere diameters for liquid Cu

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 (m^2/s)$		$D_{S-E} \times 10^9 (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
1370	2.2703	2.2805	3.6472	3.2933	3.8456	3.8283	4.1231
1380	2.2689	2.2795	3.7170	3.3492	3.9192	3.9011	4.2311
1390	2.2675	2.2784	3.7889	3.4055	3.9935	3.9744	4.3403
1400	2.2661	2.2774	3.8629	3.4622	4.0685	4.0483	4.4506
1410	2.2646	2.2763	3.9391	3.5191	4.1441	4.1227	4.5622
1420	2.2631	2.2753	4.0176	3.5765	4.2203	4.1976	4.6749
1430	2.2615	2.2742	4.0982	3.6342	4.2970	4.2729	4.7888
1440	2.2599	2.2732	4.1812	3.6922	4.3746	4.3489	4.9038

Table 4.8 Self-diffusion coefficients and hard sphere diameters for liquid Ga

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 (m^2/s)$		$D_{S-E} \times 10^9 (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
330	2.5848	2.5622	1.5925	1.9541	1.4417	1.4544	1.9937
335	2.5822	2.5596	1.6470	2.0146	1.4990	1.5123	2.0452
340	2.5797	2.5571	1.7022	2.0757	1.5573	1.5711	2.0964
345	2.5772	2.5546	1.7580	2.1374	1.6165	1.6308	2.1473
350	2.5747	2.5521	1.8145	2.1997	1.6764	1.6913	2.1981
355	2.5722	2.5496	1.8716	2.2625	1.7372	1.7526	2.2485
360	2.5697	2.5471	1.9293	2.3259	1.7988	1.8148	2.2986
365	2.5673	2.5446	1.9877	2.3899	1.8612	1.8778	2.3484

Table 4.9 Self-diffusion coefficients and hard sphere diameters for liquid Hg

Temp (K)	$\sigma_{Calculated}$ (A^o)	$\sigma_{Protopapas}$ (A^o)	$D_{Corr}^{Enskog} \times 10^9$ (m²/s)		$D_{S-E} \times 10^9$ (m²/s)		$D_{Expt} \times 10^9$ (m²/s)
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
270	2.7628	2.7722	1.3106	1.2250	1.2626	1.2583	1.2938
290	2.7488	2.7584	1.4980	1.4046	1.4722	1.4671	1.4732
310	2.7355	2.7450	1.6914	1.5914	1.6924	1.6865	1.6496
330	2.7227	2.7321	1.8893	1.7848	1.9214	1.9147	1.8219
350	2.7104	2.7196	2.0905	1.9842	2.1579	2.1506	1.9890
370	2.6988	2.7075	2.2939	2.1891	2.4026	2.3949	2.1520

Table 4.10 Self-diffusion coefficients and hard sphere diameters for liquid Pb

Temp (K)	$\sigma_{Calculated}$ (A^o)	$\sigma_{Protopapas}$ (A^o)	$D_{Corr}^{Enskog} \times 10^9$ (m²/s)		$D_{S-E} \times 10^9$ (m²/s)		$D_{Expt} \times 10^9$ (m²/s)
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
630	3.0488	3.0647	1.9773	1.7671	1.7516	1.7426	2.6160
650	3.0423	3.0584	2.1059	1.8847	1.9146	1.9045	2.9189
670	3.0357	3.0522	2.2379	2.0047	2.0838	2.0726	3.2350
690	3.0293	3.0462	2.3730	2.1272	2.2594	2.2469	3.5640
710	3.0229	3.0402	2.5113	2.2520	2.4409	2.4270	3.9053
730	3.0165	3.0343	2.6526	2.3791	2.6282	2.6128	4.2578
750	3.0102	3.0285	2.7968	2.5083	2.8211	2.8040	4.6207
770	3.0039	3.0227	2.9439	2.6397	3.0192	3.0004	4.9930
790	2.9977	3.0171	3.0936	2.7731	3.2228	3.2021	5.3749
810	2.9915	3.0115	3.2460	2.9084	3.4312	3.4085	5.7645

Table 4.11 Self-diffusion coefficients and hard sphere diameters for liquid K

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 \, (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
350	4.1207	4.1207	4.1055	4.1061	3.6722	3.6722	4.3960
370	4.1081	4.1058	4.7104	4.7656	4.2569	4.2593	5.2990
390	4.0958	4.0912	5.3475	5.4639	4.8784	4.8838	6.3370
410	4.0839	4.0770	6.0146	6.1991	5.5319	5.5412	7.4336
430	4.0724	4.0632	6.7094	6.9693	6.2141	6.2282	8.5980
450	4.0613	4.0496	7.4295	7.7727	6.9255	6.9454	9.8179
470	4.0505	4.0364	8.1730	8.6077	7.6624	7.6892	11.0840
490	4.0402	4.0234	8.9376	9.4727	8.4242	8.4593	12.3910

Table 4.12 Self-diffusion coefficients and hard sphere diameters for liquid Li

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 \, (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
465	2.7115	2.7116	7.4205	7.4150	6.5301	6.5299	6.4489
485	2.7070	2.7042	8.4190	8.6004	7.1900	7.1975	7.3301
505	2.7025	2.6969	9.4781	9.8628	7.8698	7.8861	8.2476
525	2.6982	2.6898	10.5965	11.1997	8.5676	8.5942	9.1969
545	2.6939	2.6829	11.7730	12.6085	9.2840	9.3223	10.1740
565	2.6898	2.6760	13.0064	14.0869	10.0186	10.0699	11.1740
585	2.6857	2.6693	14.2953	15.6322	10.7678	10.8338	12.1950
605	2.6817	2.6627	15.6383	17.2423	11.5315	11.6136	13.2320

Table 4.13 Self-diffusion coefficients and hard sphere diameters for liquid Na

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9$ (m²/s)		$D_{S-E} \times 10^9$ (m²/s)		$D_{Expt} \times 10^9$ (m²/s)
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
390	3.3313	3.3246	4.4786	4.6857	4.0145	4.0226	4.7828
400	3.3257	3.3191	4.8046	5.0140	4.3353	4.3439	5.1728
420	3.3145	3.3083	5.4895	5.6972	5.0119	5.0212	5.9834
440	3.3033	3.2978	6.2173	6.4143	5.7318	5.7414	6.8300
460	3.2922	3.2875	6.9871	7.1639	6.4929	6.5022	7.7070
480	3.2812	3.2774	7.7973	7.9445	7.2956	7.3040	8.6100
500	3.2702	3.2676	8.6467	8.7545	8.1359	8.1425	9.5330

Table 4.14 Self-diffusion coefficients and hard sphere diameters for liquid In

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9$ (m²/s)		$D_{S-E} \times 10^9$ (m²/s)		$D_{Expt} \times 10^9$ (m²/s)
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
450	2.8773	2.8935	2.1291	1.8847	1.9035	1.8928	1.8890
470	2.8680	2.8853	2.3340	2.0620	2.1213	2.1087	2.1225
490	2.8588	2.8772	2.5466	2.2446	2.3478	2.3328	2.3612
510	2.8498	2.8693	2.7666	2.4321	2.5827	2.5651	2.6046
530	2.8408	2.8616	2.9936	2.6244	2.8254	2.8049	2.8526
550	2.8319	2.8540	3.2273	2.8213	3.0757	3.0519	3.1032
570	2.8231	2.8465	3.4673	3.0225	3.3332	3.3058	3.3559
590	2.8144	2.8392	3.7134	3.2279	3.5977	3.5663	3.6100

Table 4.15 Self-diffusion coefficients and hard sphere diameters for liquid Rb

Temp (K)	$\sigma_{Calculated}$ (A^0)	$\sigma_{Protopapas}$ (A^0)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
375	4.3643	4.3672	3.9896	3.9410	3.9259	3.9234	4.6304
385	4.3554	4.3591	4.2401	4.1764	4.2151	4.2116	4.9612
395	4.3466	4.3511	4.4970	4.4166	4.5136	4.5090	5.2972
405	4.3378	4.3432	4.7600	4.6614	4.8193	4.8133	5.6376
415	4.3291	4.3354	5.0291	4.9107	5.1340	5.1266	5.9819
425	4.3204	4.3277	5.3040	5.1643	5.4559	5.4468	6.3296
445	4.3033	4.3125	5.8706	5.6840	6.1219	6.1087	7.0329
465	4.2863	4.2977	6.4586	6.2195	6.8174	6.7993	7.7439

Table 4.16 Self-diffusion coefficients and hard sphere diameters for liquid Sn

Temp (K)	$\sigma_{Calculated}$ (A^0)	$\sigma_{Protopapas}$ (A^0)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
530	2.9288	2.9313	2.0913	2.0506	1.9253	1.9236	2.6070
550	2.9184	2.9242	2.3112	2.2155	2.1622	2.1580	2.8498
570	2.9079	2.9172	2.5455	2.3846	2.4124	2.4047	3.0900
590	2.8972	2.9104	2.7943	2.5578	2.6757	2.6636	3.3440
610	2.8862	2.9037	3.0579	2.7350	2.9519	2.9342	3.5947
630	2.8751	2.8970	3.3365	2.9159	3.2411	3.2165	3.8460
650	2.8638	2.8905	3.6303	3.1005	3.5423	3.5096	4.0970
660	2.8580	2.8873	3.7829	3.1941	3.6976	3.6601	4.2230

Table 4.17 Self-diffusion coefficients and hard sphere diameters for liquid Tl

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
525	3.0013	3.0146	1.4081	1.2592	1.2140	1.2086	1.3925
550	2.9912	3.0061	1.5681	1.3921	1.3950	1.3881	1.6868
600	2.9712	2.9897	1.9124	1.6715	1.7904	1.7794	2.3591
610	2.9672	2.9865	1.9850	1.7295	1.8747	1.8626	2.5063
620	2.9632	2.9833	2.0588	1.7881	1.9606	1.9474	2.6574
630	2.9593	2.9801	2.1338	1.8474	2.0481	2.0338	2.8124
640	2.9553	2.9770	2.2101	1.9073	2.1373	2.1217	2.9711

Table 4.18 Self-diffusion coefficients and hard sphere diameters for liquid Zn

Temp (K)	$\sigma_{Calculated}$ (A°)	$\sigma_{Protopapas}$ (A°)	$D_{Corr}^{Enskog} \times 10^9 \, (m^2/s)$		$D_{S-E} \times 10^9 \, (m^2/s)$		$D_{Expt} \times 10^9 (m^2/s)$
			$\sigma_{Calculated}$	$\sigma_{Protopapas}$	$\sigma_{Calculated}$	$\sigma_{Protopapas}$	
700	2.5001	2.4572	1.5545	2.4995	1.3515	1.3751	2.1411
720	2.4975	2.4528	1.6435	2.6581	1.4705	1.4973	2.3944
740	2.4949	2.4484	1.7334	2.8201	1.5943	1.6246	2.6616
780	2.4900	2.4399	1.9147	3.1540	1.8552	1.8933	3.2357
800	2.4877	2.4357	2.0058	3.3257	1.9918	2.0344	3.5416
820	2.4855	2.4315	2.0971	3.5005	2.1325	2.1798	3.8594
840	2.4833	2.4274	2.1884	3.6782	2.2770	2.3295	4.1885
860	2.4813	2.4234	2.2795	3.8588	2.4253	2.4833	4.5284
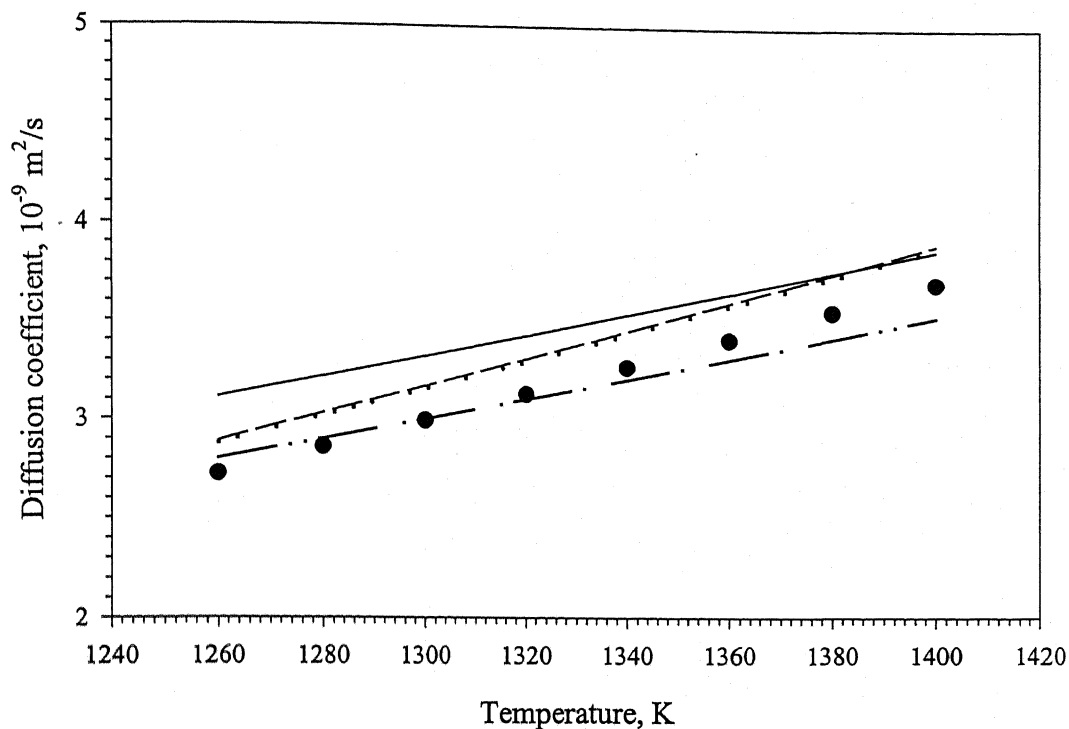
Fig 4.1 Self-diffusion coefficients of liquid Silver as a function of temperaure.
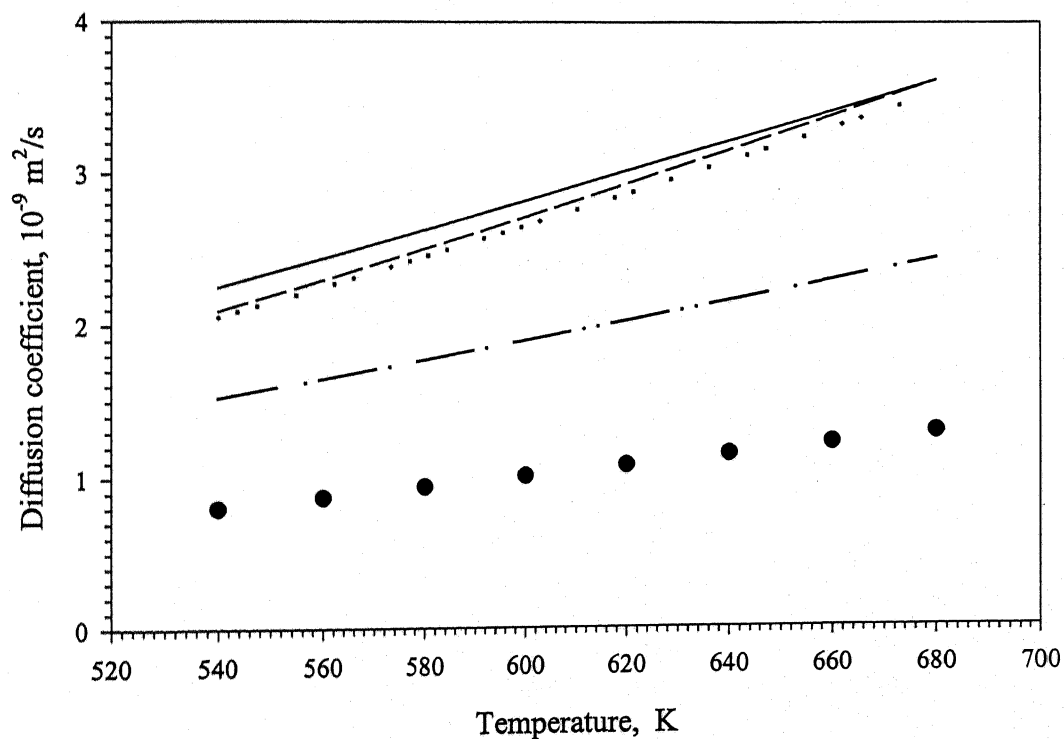
Fig 4.2 Self-diffusion coefficients of liquid Bismuth as a function of temperature.
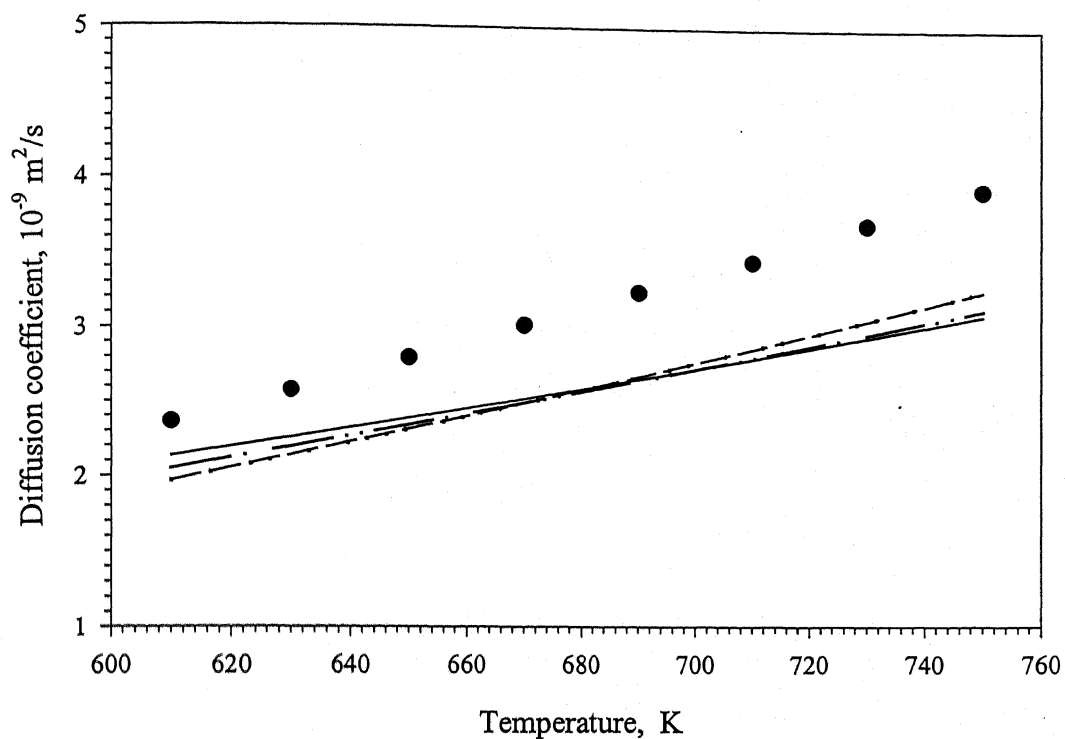
Fig 4.3 Self-diffusion coefficients of liquid Cadmium as a function of temperature.
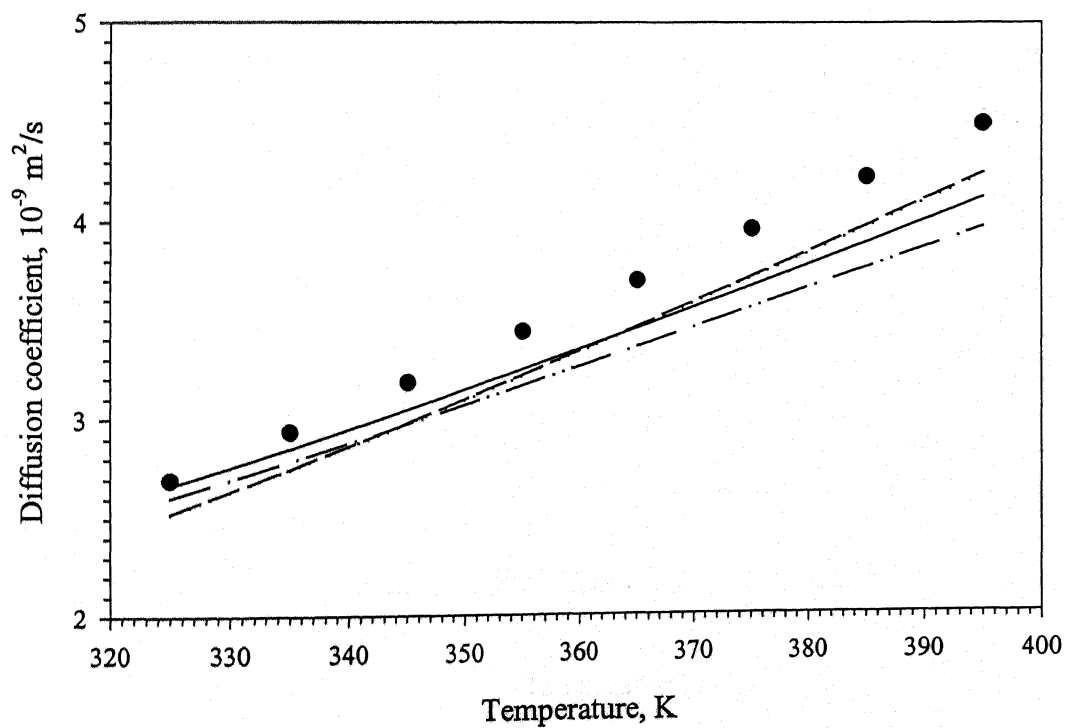
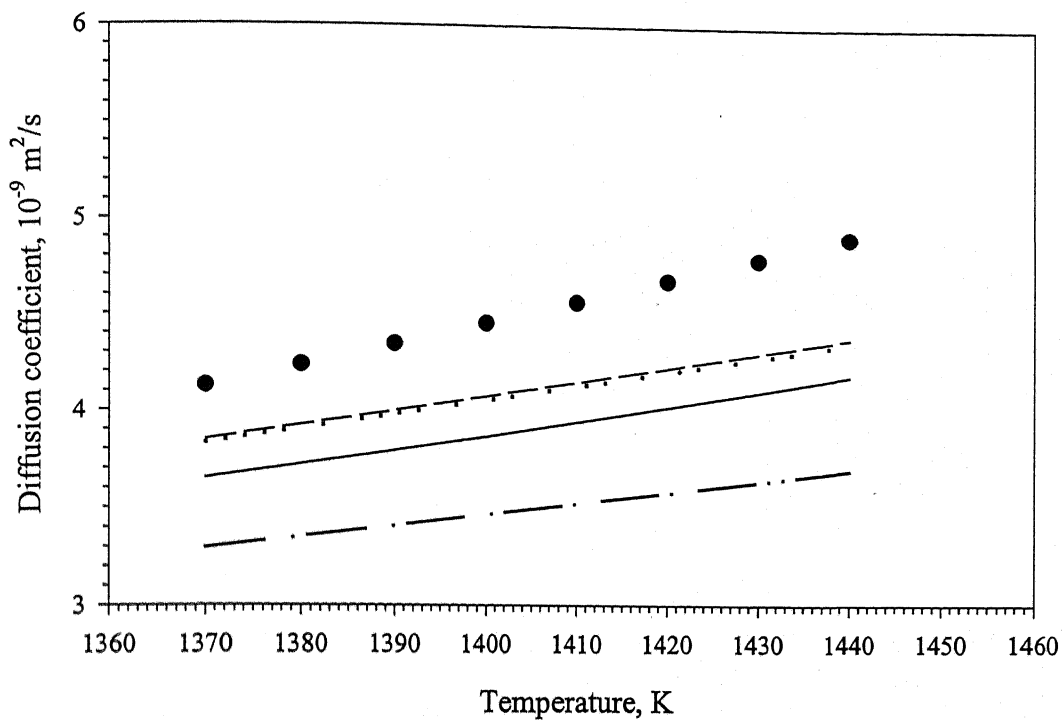Fig 4.4 Self-diffusion coefficients of liquid Caesium as a function of temperature.

Fig 4.5 Self-diffusion coefficients of liquid Copper as a function of temperature.
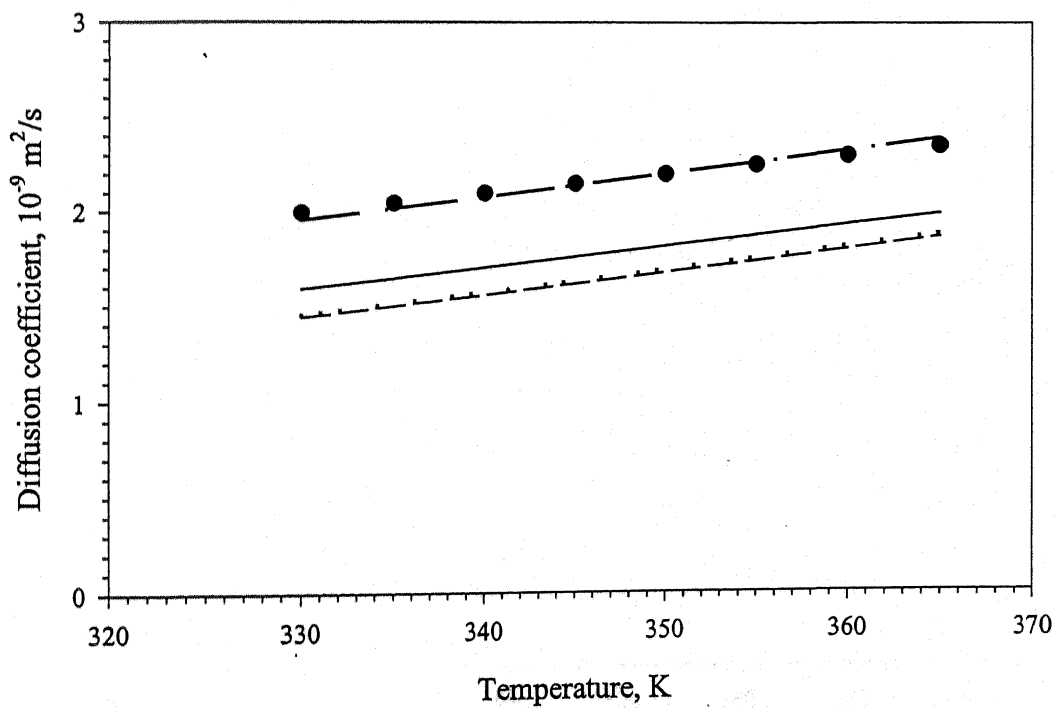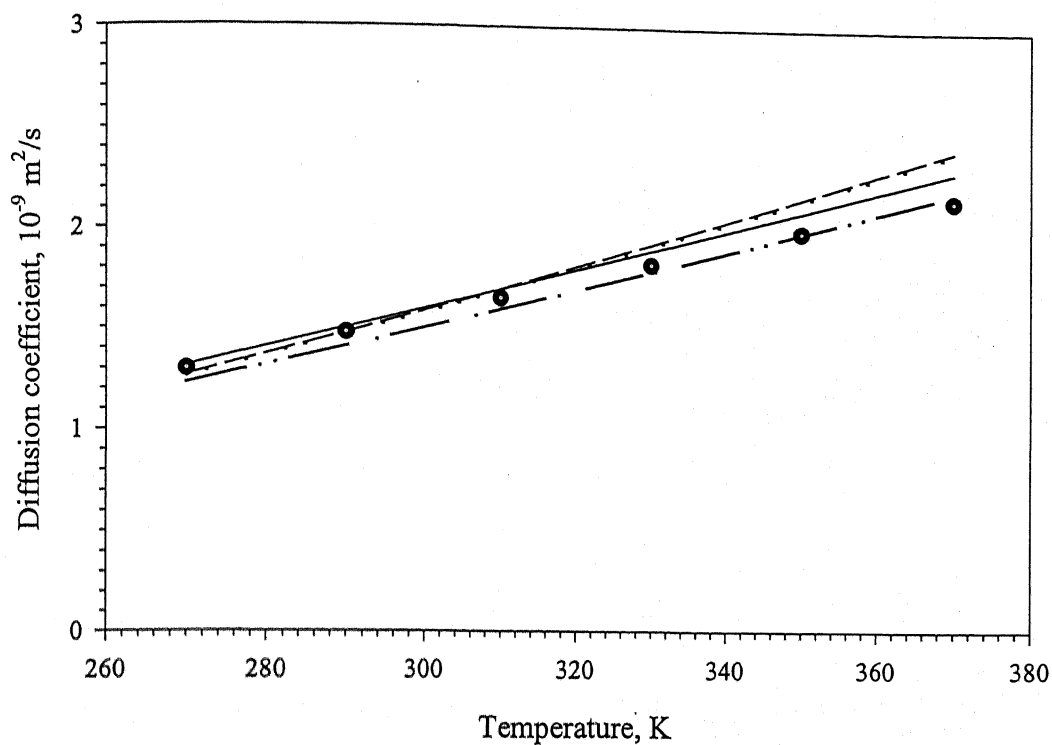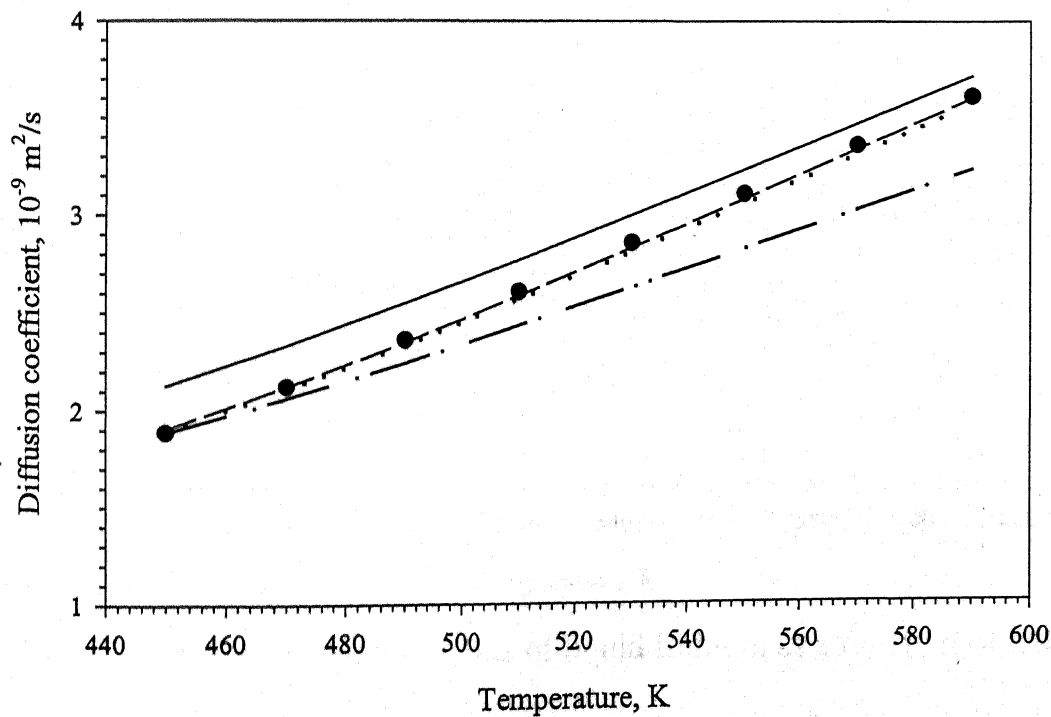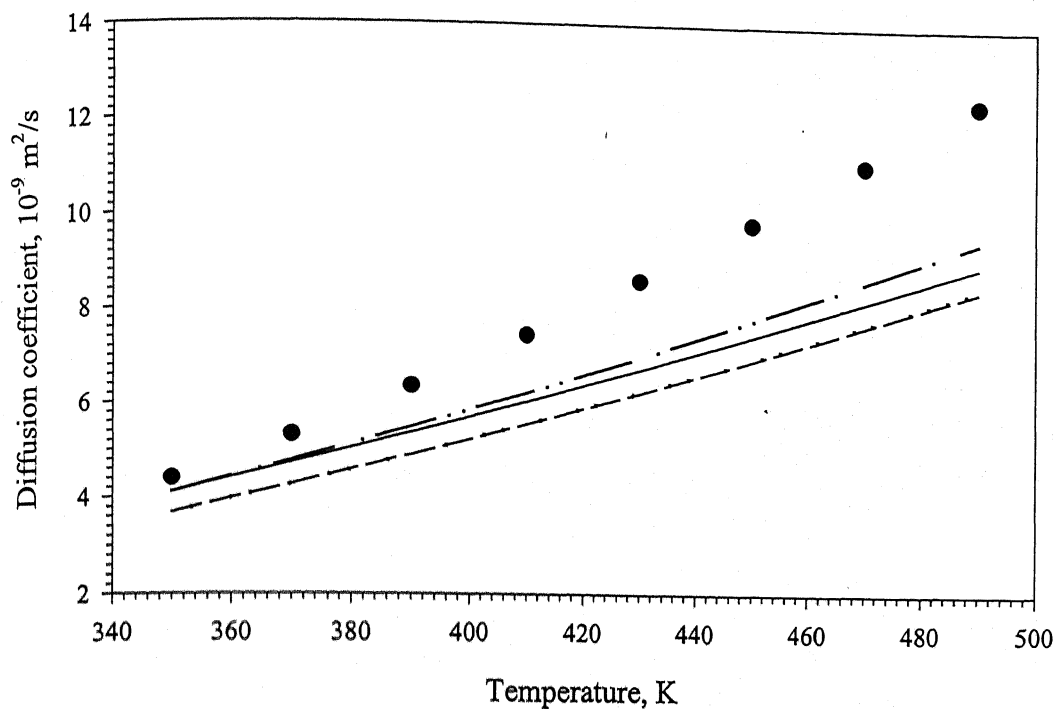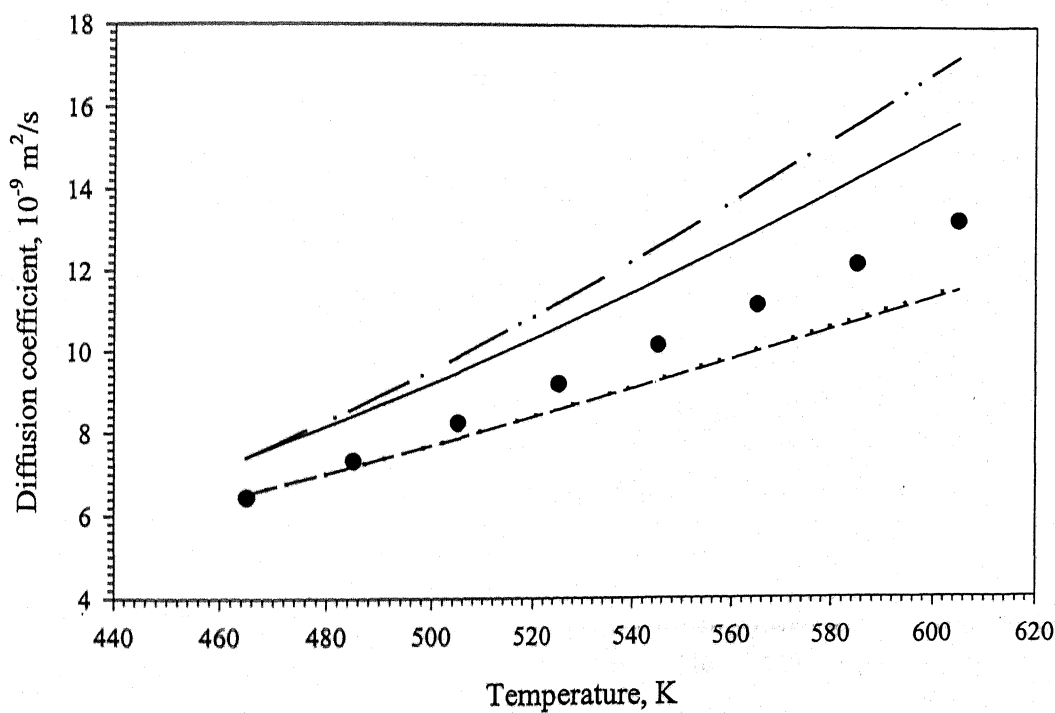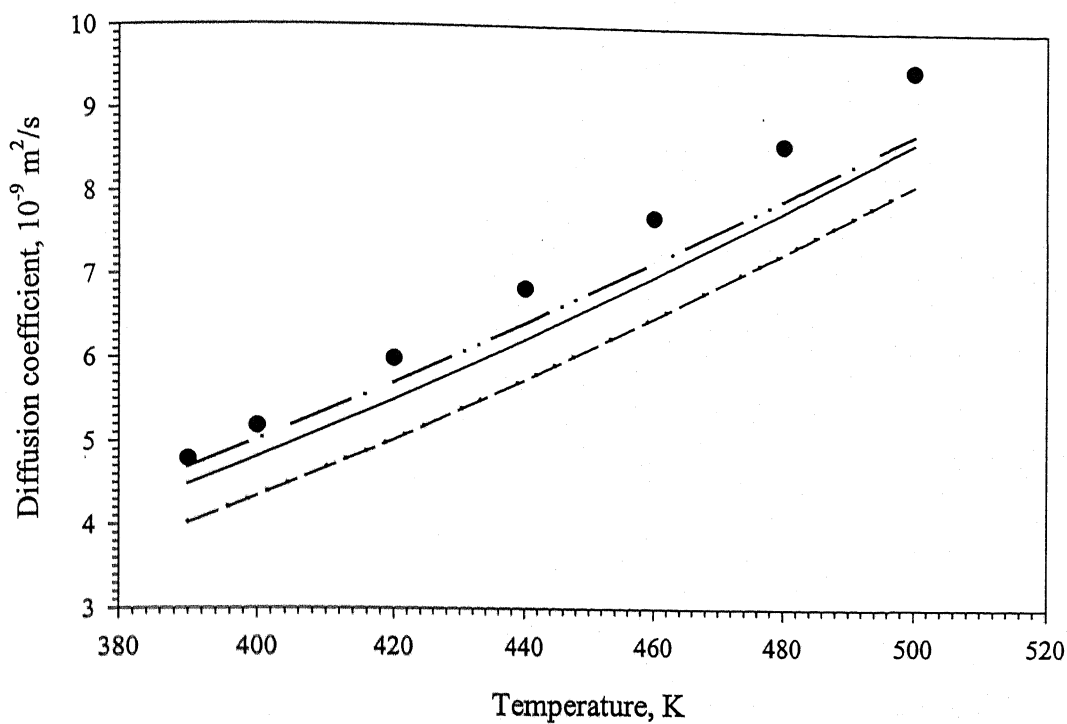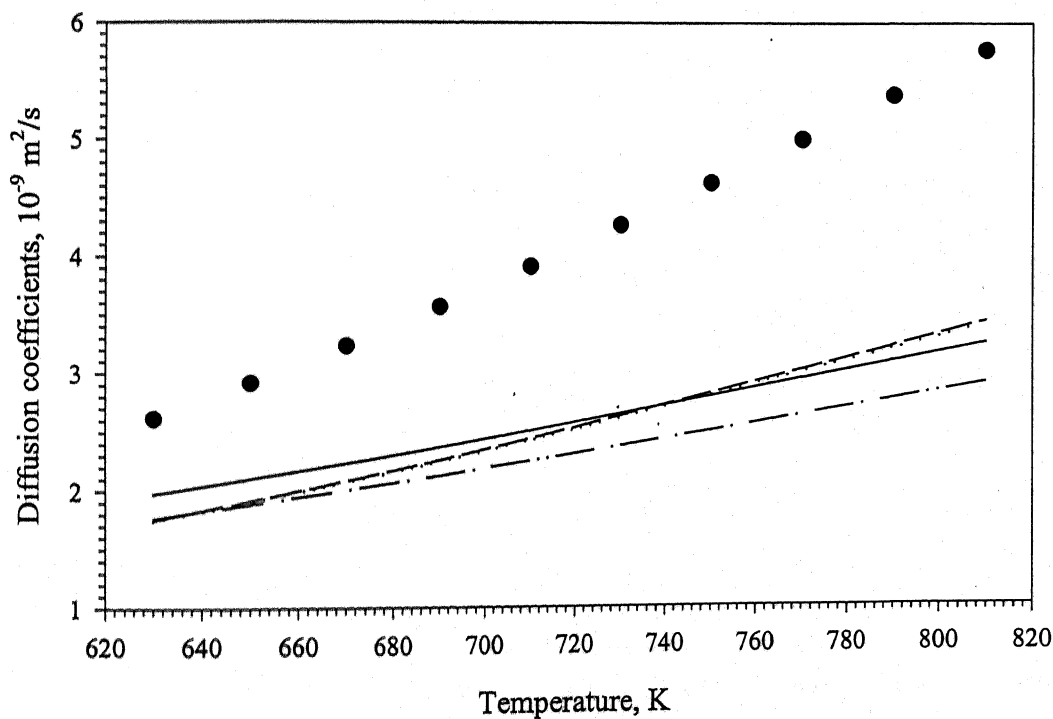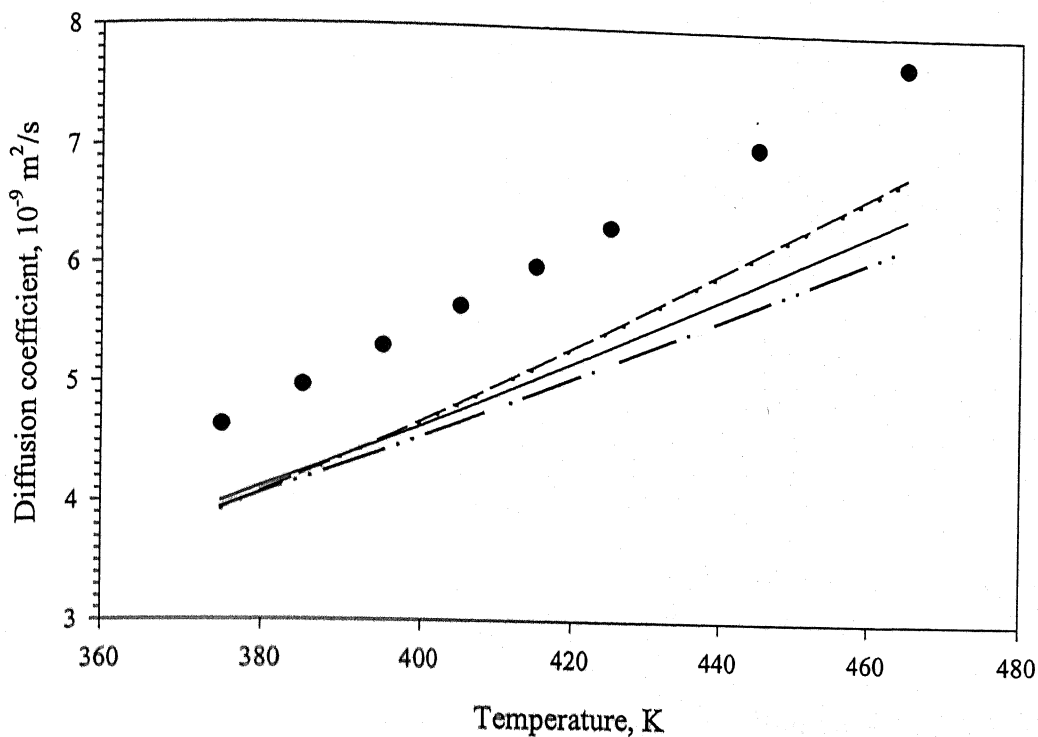

Fig 4.6 Self-diffusion coefficients of liquid Gallium as a function of temperature.

Fig 4.7 Self-diffusion coefficients of liquid Mercury as a function of temperature.

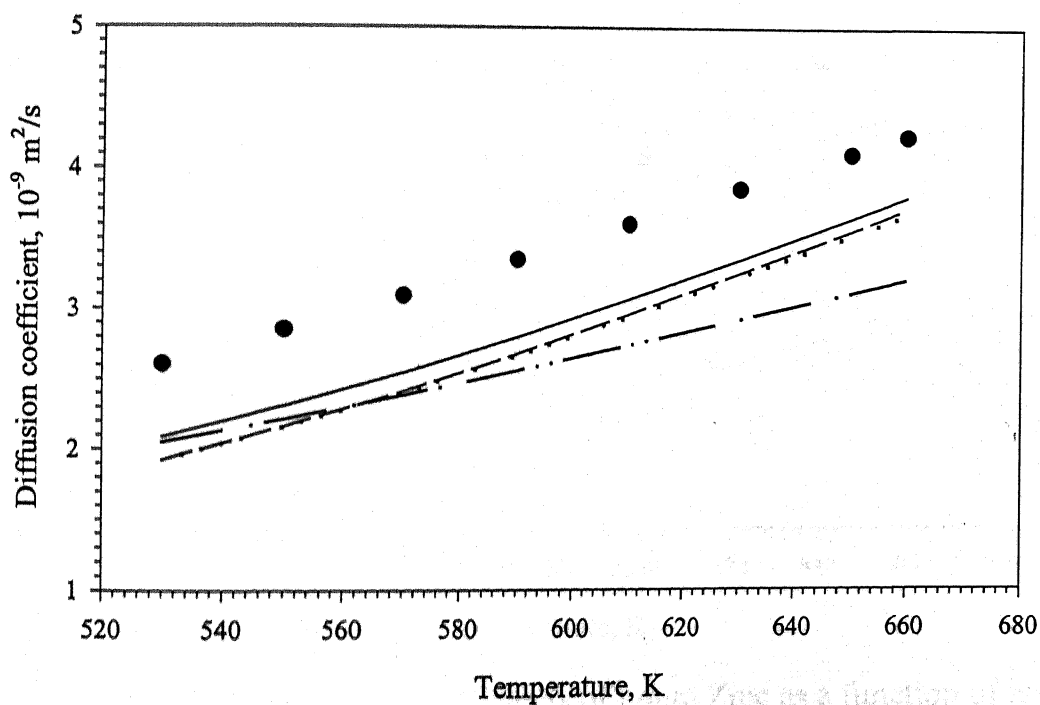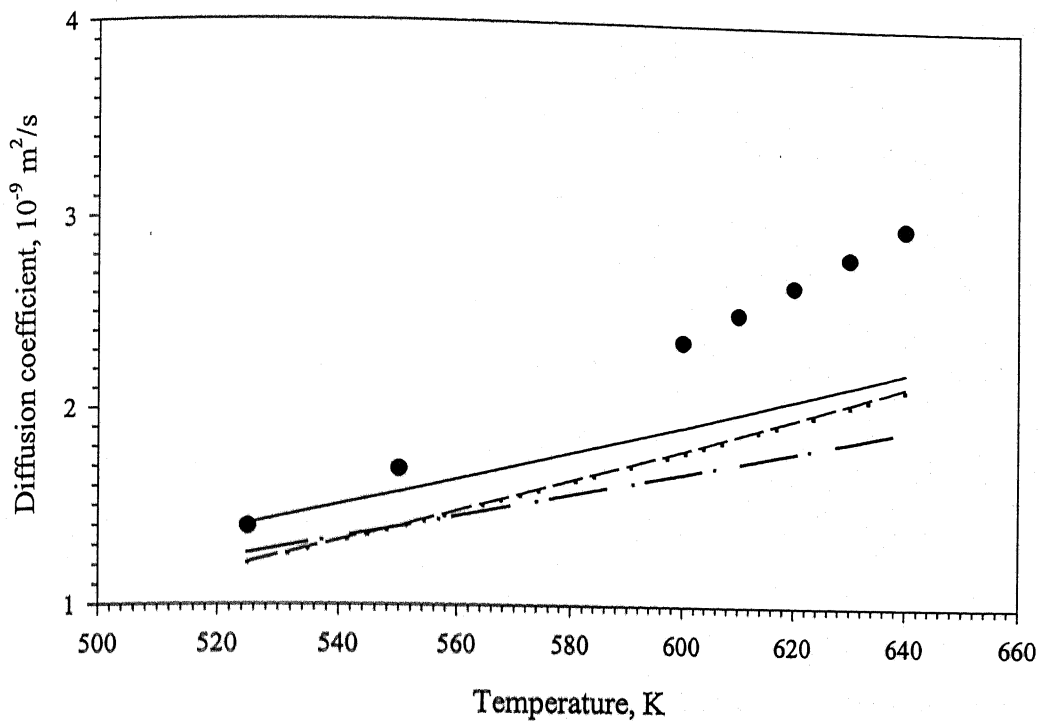Fig 4.8 Self-diffusion coefficients of liquid Indium as a function of temperature.

Fig 4.9 Self-diffusion coefficients of liquid Potassium as a function of temperature.

Fig4.10 Self-diffusion coefficients of liquid Lithium as a function of temperature.

Fig 4.11 Self-diffusion coefficients of liquid Sodium as a function of temperature.

Fig 4.12 Self-diffusion coefficients of liquid Lead as a function of temperature.

Fig 4.13 Self-diffusion coefficients of liquid Rubidium as a function of temperature.

Fig 4.14 Self-diffusion coefficients of liquid Tin as a function of temperature.

Fig 4.15 Self-diffusion coefficients of liquid Thallium as a function of temperature.
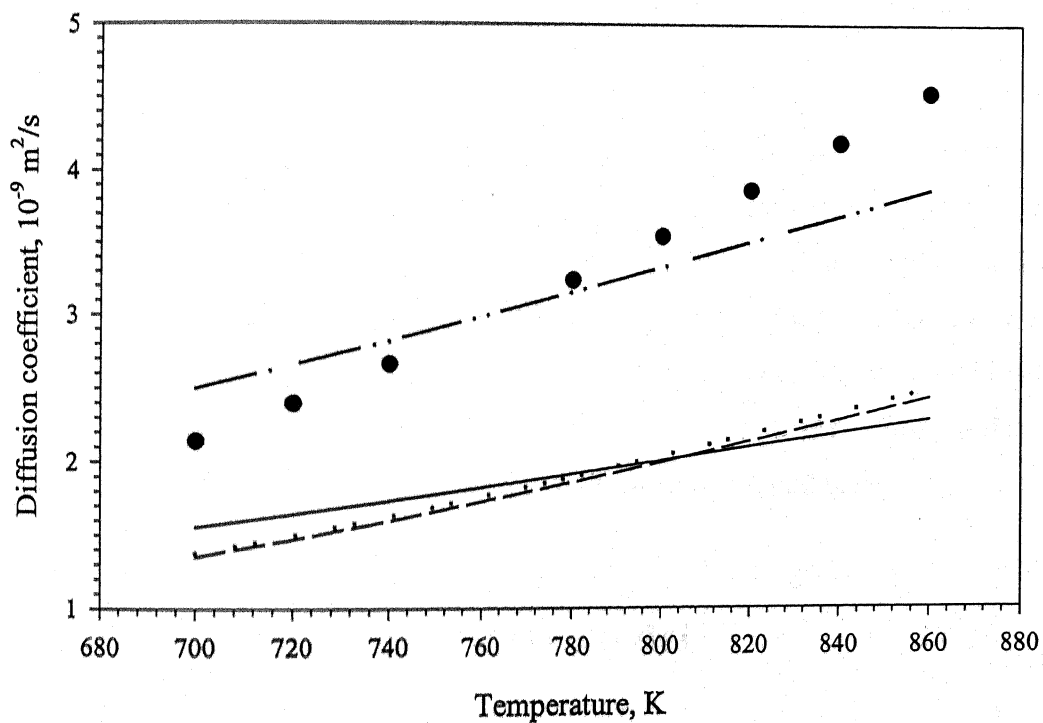

Fig 4.16 Self-diffusion coefficients of liquid Zinc as a function of temperature.

predictability of this model is to reconsider the assignment of a suitable value to size of the diffusing species, *R*. So, in this regard, Goldschmidt atomic diameter was replaced by the effective hard sphere diameters, which were calculated using the approach outlined by Protopapas and Parlee and from the experimental viscosity data.

It was observed that the predictions of the diffusion values by these two diameters are almost identical. This points to the reduced sensitivity the Stokes-Einstein model to the choice of the characteristic diameter. It was shown earlier (Chauhan, 2000) that within the context of the Stokes- Einstein model, the temperature-independent. Gold schmidt diameter consistently under predicts the diffusion coefficient and the use of the temperature dependent Protopapas-Parlee diameter and diameter calculated from the viscosity data improves predictions. Thus, while incorporating the temperature dependence of the characteristic diameter helps in improving the Stokes-Einstein model predictions, neither of the two diameters considered here can capture the temperature dependence of diffusivities adequately.

Finally, it is appropriate to point out here that for estimating the Protopapas and Parlee diameter, one needs only the melting point temperature and the corresponding value of density. On the other hand, if one were to use the viscosity data as illustrated in this work, the parameters A, B and C have to be determined for each metal. However, it is worth nothing that the Protopapas and Parlee diameter was obtained by using diffusivity data and hence is to be regarded more as a fit to the diffusivity data rather than as a method for a priori determination of diffusivity of liquid metals.

4.4 Corresponding states model

Chapman (1966) has shown that it was possible to collapse viscosity data onto a single curve by the adjustment of one microscopic parameter (ε). It is found that this empirically evaluated parameter has some fundamental significance. Pasternak (1967) has obtained a correlation for self-diffusion coefficient and viscosity of liquid metals
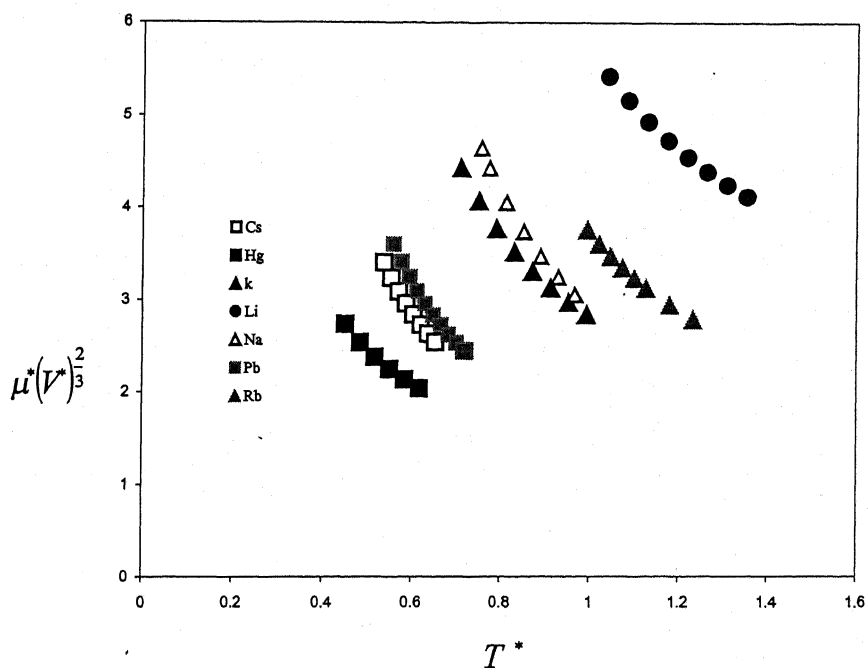
Fig 4.17 Plot of $\mu^*\left(V^*\right)^{\frac{2}{3}}$ vs. T^* using long-range oscillatory potentials (Johnson et al., 1964).

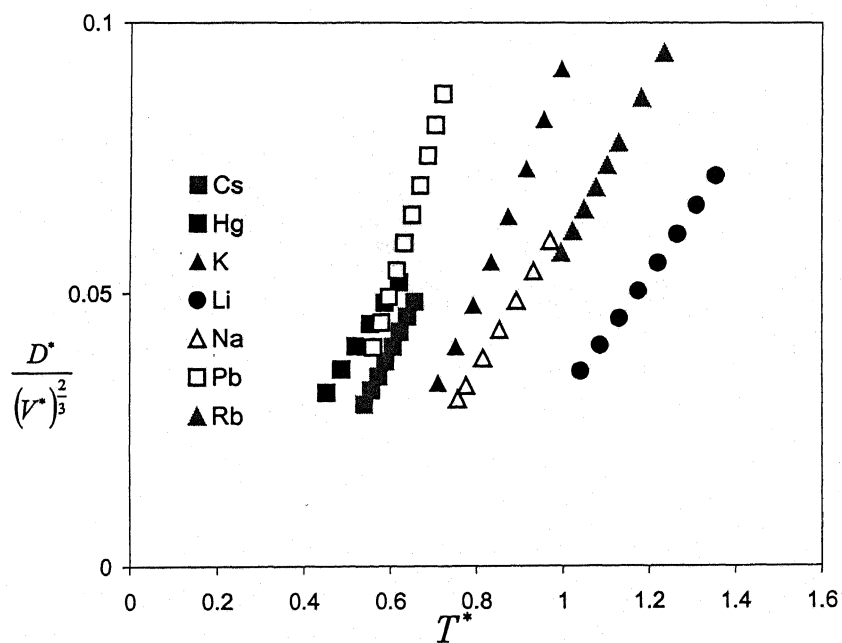Fig 4.18 Plot of $\dfrac{D^*}{\left(V^*\right)^{\frac{2}{3}}}$ vs. T^* using long-range oscillatory potentials (Johnson et al., 1964).
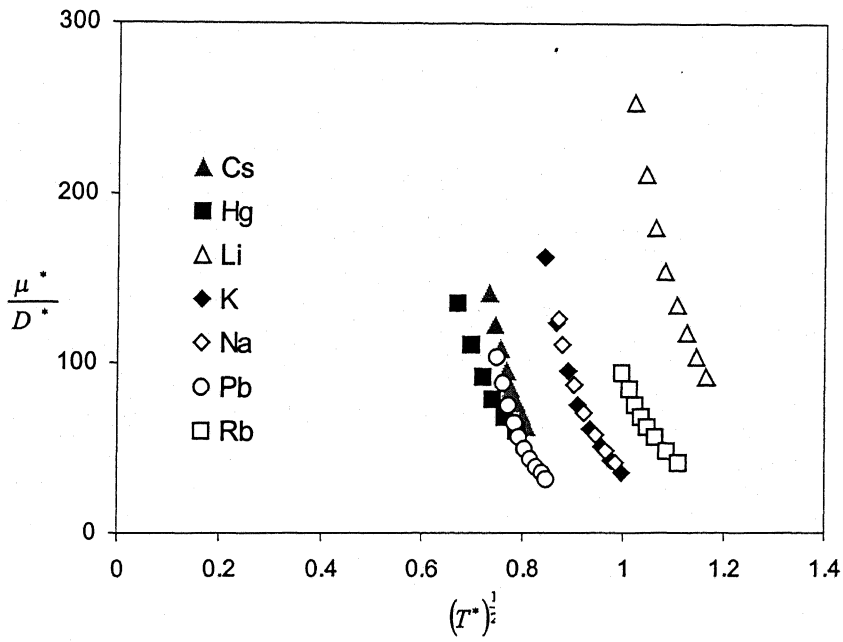
Fig 4.19 Plot of $\dfrac{\mu^*}{D^*}$ vs. $\left(T^*\right)^{\frac{1}{2}}$ using long-range oscillatory potentials (Johnson et al., 1964).
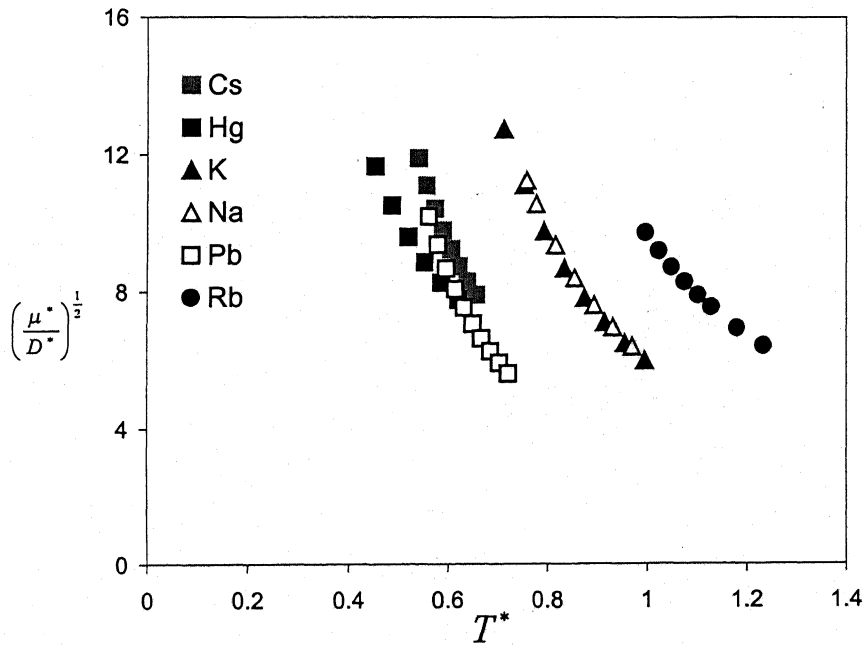

Fig 4.20 Plot of $\left(\dfrac{\mu^*}{D^*}\right)^{\frac{1}{2}}$ vs. T^* using long-range oscillatory potentials (Johnson et al., 1964)
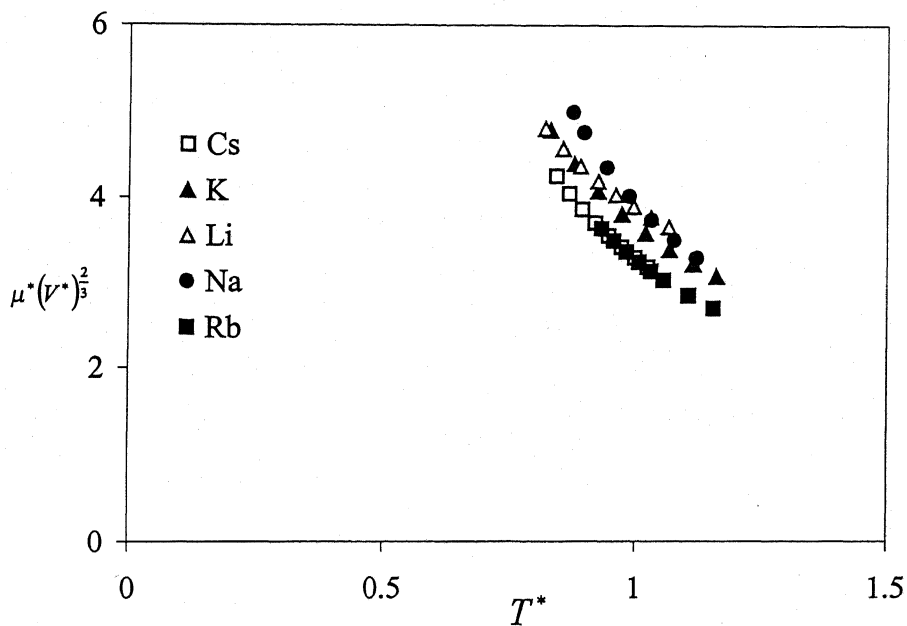
Fig 4.21   Plot of $\mu^*\left(V^*\right)^{\frac{2}{3}}$ vs. T^* using pseudo potential parameters
(Ranganathan and Pathak, 1994).

Fig 4.22   Plot of $\dfrac{D^*}{\left(V^*\right)^{\frac{2}{3}}}$ vs. T^* using pseudo potential parameters
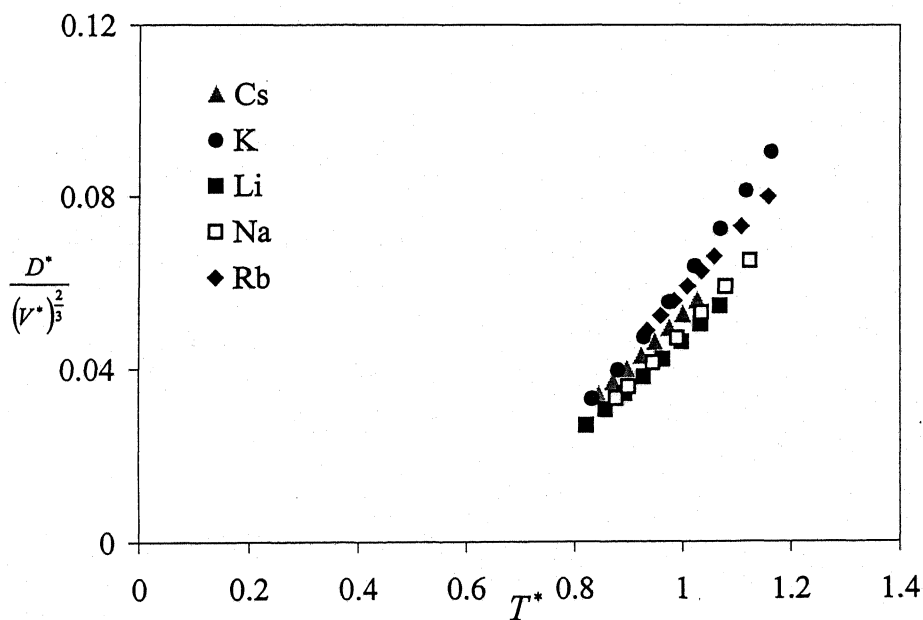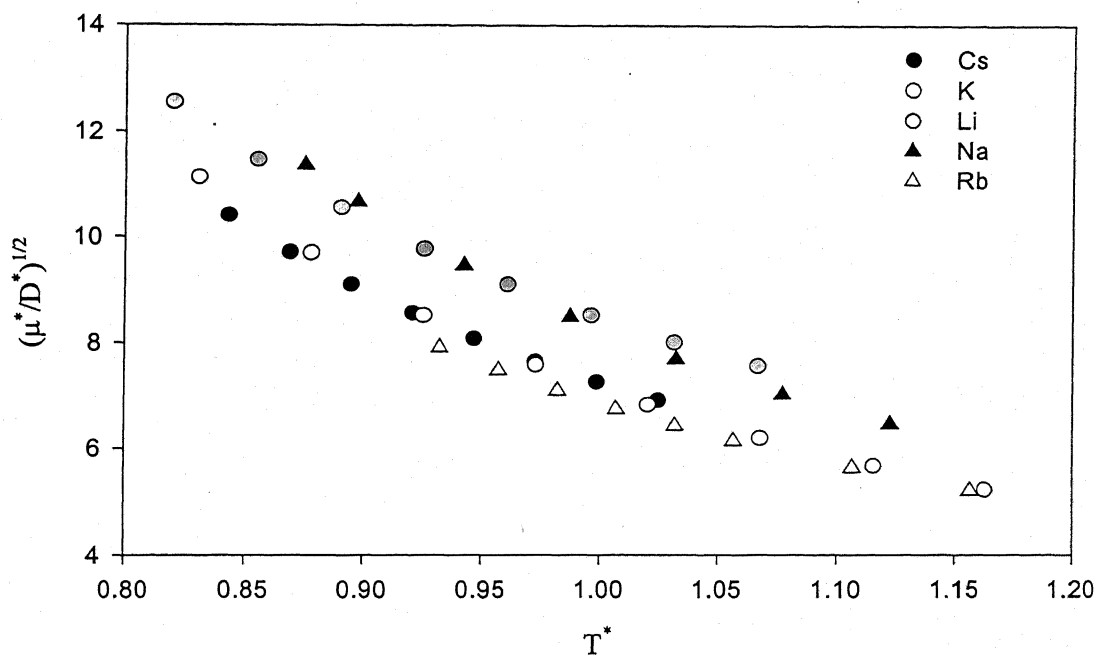
(Ranganathan and Pathak, 1994).

Fig 4.23 Plot of $(\mu^*/D^*)^{1/2}$ vs T^* using pseudo potential parameters (Ranganathan and Pathak, 1994).
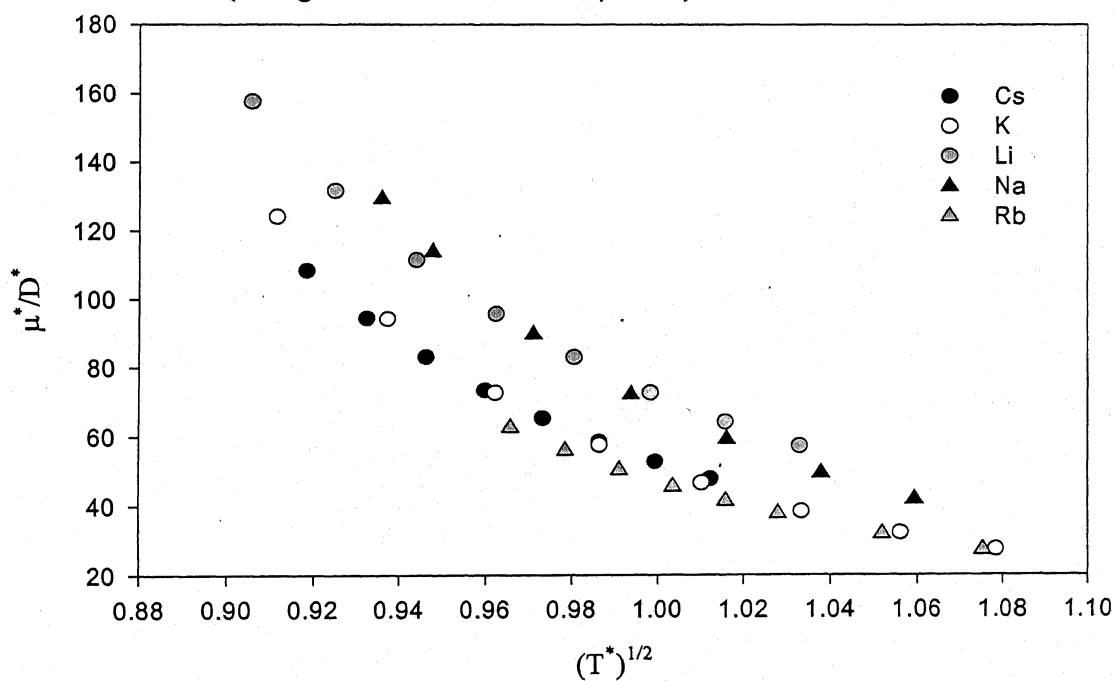

Fig 4.24 Plot of μ^*/D^* vs. T^* using pseudo potential parameters (Ranganathan and Pathak, 1994).

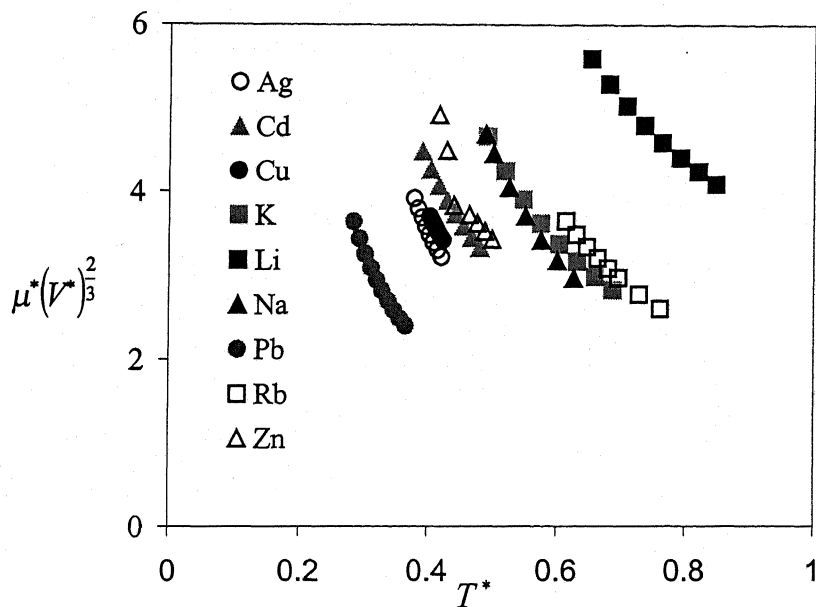Fig 4.25   Plot of $\mu^*\left(V^*\right)^{\frac{2}{3}}$ vs. T^* using Lennard-Jones (m-n) potential parameters (Zhen and Davies, 1983).
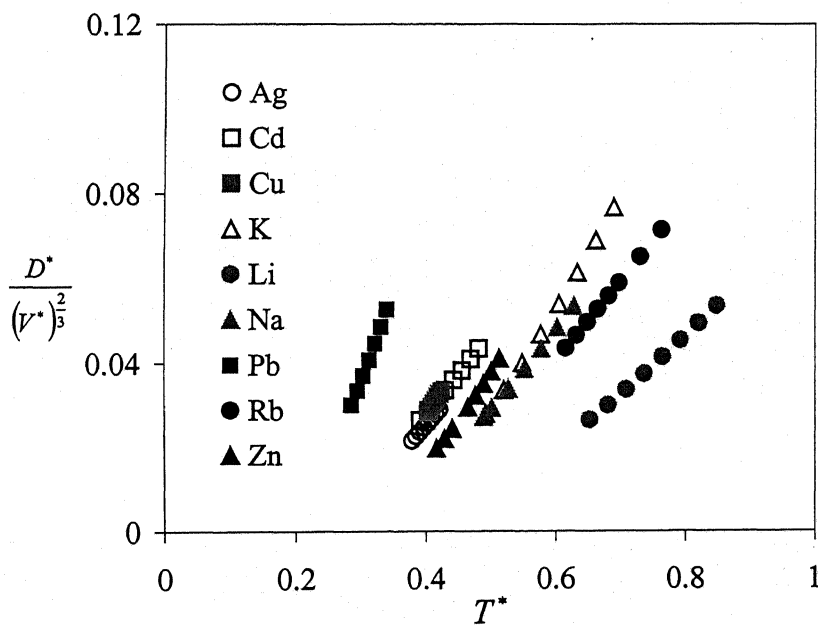
Fig 4.26   Plot of $\dfrac{D^*}{\left(V^*\right)^{\frac{2}{3}}}$ vs. T^* using Lennard-Jones (m-n) potential parameters (Zhen and Davies, 1983).
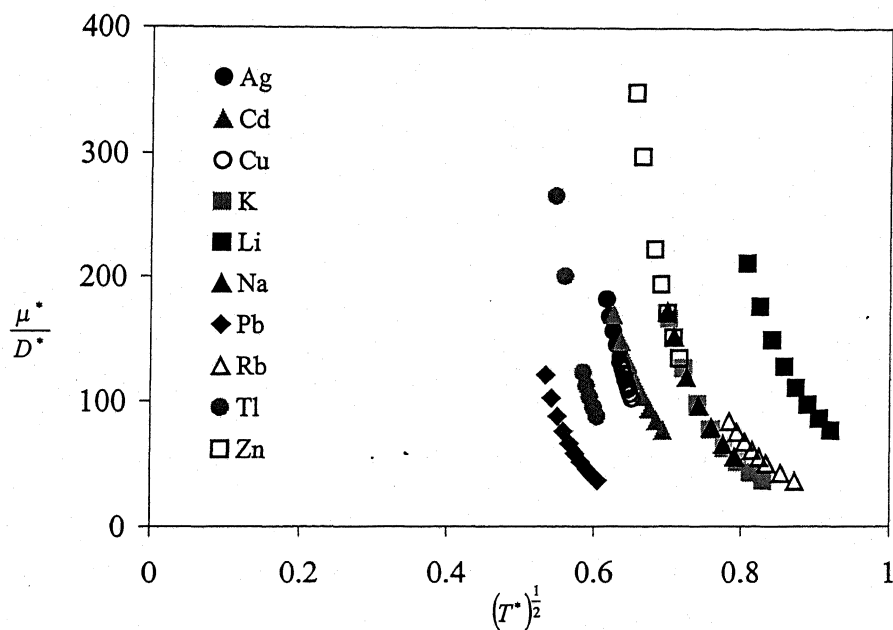
Fig 4.27 Plot of $\dfrac{\mu^*}{D^*}$ vs. $\left(T^*\right)^{\frac{1}{2}}$ using Lennard-Jones (m-n) potential parameters (Zhen and Davies, 1983).
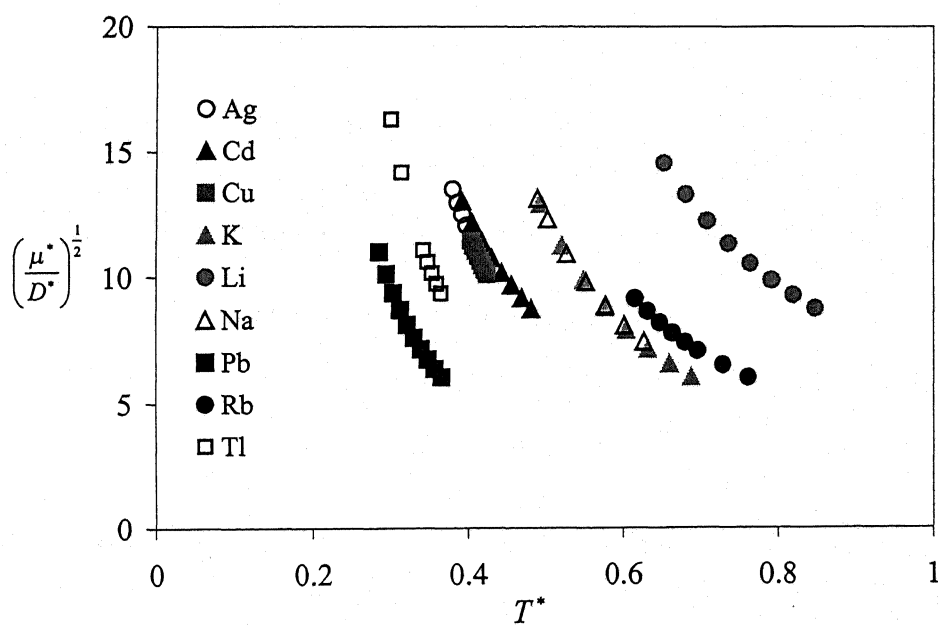

Fig 4.28 Plot of $\left(\dfrac{\mu^*}{D^*}\right)^{\frac{1}{2}}$ vs. using Lennard-Jones (m-n) potential parameters (Zhen and Davies, 1983).

using Helfand and Rice (1960) model and the parameters, which were obtained by Chapman (1966). The Chapman's correlation was tested with various potential parameters, which were obtained from different types of potentials. Lennard-Jones (m-n) (Zhen and Davies, 1983), long-range oscillatory (Johnson et al., 1964) and pseudo potentials (Ranganathan and Pathak, 1994) were chosen in this approach. Different combinations of reduced quantities were calculated and were plotted against reduced temperatures. The trends of such plots are shown in figures (4.17-4.28).

We restricted our selves to certain metals for which both viscosity and diffusivity data is available. The plots of volume dependency of reduced viscosity and reduced diffusivity (fig 4.17 and 4.18) using long-range oscillatory potential parameters, shows that liquid metals do fall on the single curve, but the plots of ratio of reduced viscosity and reduced diffusivity (fig 4.19-4.20) show that the liquid metals Hg, Cs, Pb do fall onto one curve where as K and Na follow another curve. The reduced quantities, calculated using the pseudo potential parameters (Ranganathan and Pathak, 1994) were shown (fig 4.21-4.24) to follow the same trend irrespective of combinations of reduced quantities. The curves obtained using pseudo potentials are close to each other than those obtained from the other potentials. The plots of $\mu^*\left(V^*\right)^{\frac{2}{3}}$ vs. T^* and $\dfrac{D^*}{\left(V^*\right)^{\frac{2}{3}}}$ vs. T^* (fig 4.25 and 4.26) show that the liquid metals are not falling on the same single curve. But the plot of $\dfrac{\mu^*}{D^*}$ vs. $\left(T^*\right)^{\frac{1}{2}}$ shows that the liquid metals Zn, Na, and K collapse onto the same line where as liquid Rb tends to fall on that curve. The plot of $\left(\dfrac{\mu^*}{D^*}\right)^{\frac{1}{2}}$ vs. T^* shows that only Na and K are falling on the same line and the rest are falling on different curves.

All these potentials were used in the calculations of bulk modulus, electrical resistivity and the other thermodynamic properties of liquid metals. These parameters lead to the values which show considerable agreement with experimental values. However, it is not possible to pinpoint the exact reason for this type of behavior.

Furthermore, no potential gives potential parameters for all liquid metals. The temperature range, which we used in our calculations, is +10% of the melting temperature. So this temperature range changes from one metal to another, therefore, the reduced quantities range also varies from one metal to the other. This might be the reason why these metals do not follow the same curve, because according to definition of corresponding state principle, the reduced viscosity or diffusivity of similar substances in any thermodynamic state should be a universal function of the reduced thermodynamic properties of that state such as reduced temperature and pressure. One way to obtain such universal function is to follow the scheme outlined by Chapman (1966) and Pasternak (1967) with different types of potential parameters and then minimize the errors in correlating a universal function.

Chapter 5

CONCLUSIONS

5.1 Conclusions

In this work, the efficacy of a hard sphere diameter, inferred from viscosity-temperature data, in predicting the self-diffusion coefficient of liquid metals using the corrected Enskog and the Stokes-Einstein relationship has been extensively investigated. An attempt has been made to examine the applicability of the corresponding state principles for a universal correlation for viscosity and diffusivity of the metallic system. Based on the analysis reported herein, following conclusions can be drawn:

1. It has been shown that hard sphere diameter estimated from viscosity data can lead to reasonably accurate values of self-diffusion coefficients of liquid metals. The relative ease with which such viscosity data is available makes this approach attractive. However, with the above hard sphere diameters, neither the Stokes-Einstein equation nor the corrected Enskog equation are able to predict the temperature dependence of the diffusivity as strongly as observed experimentally. Nevertheless, the predictions are comparable to those obtained using the Protopapas and Parlee diameters which are inferred from diffusion data itself.

2. Liquid metals do not follow the universal curve of corresponding states model when tested with various types of potential parameters. The main difficulty appears to be in the lack of information regarding the potential parameters for the systems investigated herein.

5.2 Recommendations for future work

Further experimental work is needed to encompass many more metallic systems in terms of their viscosity and diffusivity data over a wide range of temperature as possible. This will enable the validation of the approaches employed in this work. Similarly, in order to test the applicability of the corresponding state principle in a much more through manner, it is required to evaluate the potential parameters for molten metals so that a coherent framework can be developed.

References

Alder, B.J.,Gass, D.M and Wainwright, T.E. *J.Chem.Phys.* **53** (1970) 3813.

Andersen, H.C., Chandler, D. and Weeks, J.D. *J.Chem.Phys.* **56** (1972) 3812.

Andrade, E.N.da C. and Dobbs, E.R. *Proc.Phys.Soc.* **211A** (1952) 12.

Andrde, E.N.da C. *Phil.Mag.* 17 (1934) 497.

Ascarelli,P. and Paskin, A. *Phys.Rev.* **145** (1967) 222.

Ascarelli , P.and Paskin, A. *Phys.Rev.* **165** (1968) 222.

Ascarlelli, P. *Phys.Rev.***73** (1968) 271.

Ashcroft, N.W. and Lekner, J. *Phys.Rev.* **145** (1966) 83.

Baker, J.A. and Henderson, D. *J.Chem.Phys.* **47** (1967) 4714.

Bari, A. and Jorder, R.N. *Ind.J.Pure & Appl.Phys.* **30** (1992) 256.

Bari, A., Das, T.and R.N.Jorder, *J.Non.Crstalline.Soilds.***136** (1991) 173.

Ben-Amotz , D. and Herschbach, D.R. *J.Phys.Chem.* **94** (1990) 1038.

Ben-Amotz, D. and Wills, K.G. *J.chem.Phys.* **79** (1993) 7736.

Born, M. and Green, H.S. *Proc.Roy.Soc.* **190A** (1947) 455.

Breitling, S.M and Erying, H. Liquid Metals: Chemistry and Physics (ed. S.Z.beer), ch.5, Marcel Dekker, New York, 1972.

Cahill, J.A. and Grosse, A. *J.Phys.Chem.* **69** (1965) 518.

Careri, G., Paoletti, A. and Vincentini, M. *Nuovo CIM.* **10** (1958) 1088.

Carnahan, N. and K.Starling, K. *J.Chem.Phys.* **51** (1969) 635.

Castillo, R., Villaverde, A., and J.Orozeo, J. *J.Molec.Phys.* **74** (1991) 1315.

Chapman, T.W. *J.A.I.Ch.E.* **12** (1966) 395.

Chapman, S. and Cowling, T.G. *The Mathematic Theory of Non-uniform Gases*, Cambridge University Press, New York, 1970.

Chauhan, A.S., Ravi, R. and Chhabra, R.P. *Chem.Phys.* **252** (2000) 227

Cohen, M.H. and turnbull, D. *J.Chem.Phys.* **31** (1959) 1164.

Crawly, A.F. and Thresh, H.R. *Trans.Met.Soc.A.I.M.E.* **245** (1969) 424.

Dymond, J.H. and Alder, B.J. *J.Chem.Phys.* **45** (1966) 2061.

Dymond, J.H. *Physica*.**85A** (1976) 175.

Edwards, J.T. *J.Chem.Edu.* **47** (1970) 261.

Eyrng, H., Henderson, D., Stover, B.J. and Eyring, E.M. *Statistical Mechanics and Dynamics*, John wiley &sons, New York, 1964.

Faber, T.E. *Introduction to the Theory of Liquid Metals.* p.165, Cambridge University Press, 1972.

Gebhart, E.V. andBecker, *Z.Met.* **42** (1951) 111.

Grosse, A.V. *J.Inorg.Nucl.Chem.***23** (1961) 333.

Helfand, E. and.Rice, S.A. *J.Chem.Phys.* **32** (1960) 1642.

Henderson, J. and Yang, L. *Trans.A.I.M.E.* **221** (1961) 72.

Hines, A.L. and Chung, T.W. *Met.Matt.Trans.* **27B** (1966) 29.

Hoffman, R.E. *J.Chem.Phys.* **20** (1952) 1567.

Iida, T. and Gutherie, R.I.L. *The Physical Properties of Liquid Metals.* Oxford Science Publications, 1988.

Innes, K.K. *J.Phys.Chem.* **60** (1956) 817.

Johnson, M.D., Hutchinson, P. and H.March, N. *Proc.Roy.Soc.* **282A** (1964) 283.

Khanna, K.N., A.Quayoum, A., and Kapoor,R. *Ind.J.Pure&App.Phys.* **31** (1993) 861.

Lado, F. *Molec. Phys.* **52** (1984) 871.

Landolt-Bornstein tables 5 Teil, Band a, Sprinter Verlag, (1969).

Larson, S.J., Lodding, A. and Robergh, C. *Phys.Chem.Liq.* **3** (1972) 137.

Ling, R.C. *J.Chem.Phys.* **25**(1956) 609.

Lodding, A. *Z.Naturfosch.* **11A** (1956) 200.

Longuet-Higgins, H.C., and Pople, J.A. *J.Chem.Phys.* **25** (1956) 884.

Macleod, D.B. *Proc.Phys.Soc.* **50** (1938) 788.

Mayer, R.E. and Nachtrieb, N.H. *J.Chem.Phys.* **23** (1955) 1851.

Miller, R.R. *Liquid Metals Handbook*, Atomic Energy Commission and The Department of Navy, Washington, D.C, 1952.

Murday, J.S. and Cotts, R.M. *J.Chem.Phys.* **48** (1968) 4938.

Nachtrieb, N.H., Fraga, E. and Wahl, C. *J.Phys.Chem.* **67** (1963) 2353.

Norden, A. and Lodding, A. *Z.Naturfosch.* **22A** (1967) 215.

Pasternak, A.D. and Olander, D.R. *J.A.I.Ch.E.* **13** (1967) 1052.

Percus, J.K. and Yevick, G.J. *Phys.Rev.* **110** (1958) 1

Petit, J. and Nachtrieb, N.H. *J.Chem.Phys.* **24** (1956) 1056.

Pollack, G.L. *Phys.Rev.* **23A** (1981) 2660.

Pollack, G.L and Enyeart, J.H. *Phys.Rev.* **31A** (1985) 5861.

Protopapas, P., Andersen, H.C., and Parlee, N.A.D. *J.Chem.Phys.* **59** (1973) 15.

Protopapas, P. and Parlee, N.A.D. *High.Temp.Sci.* **6** (1974) 1.

Rahman, A. *Phys.Rev.* **136** (1964) 405

Randolf, P.D. *Phys.Rev.* **134A** (1964) 1238.

Ranganathan, S., and Pathak, K.N. *J.Phys: Condens.Matter.* **6** (1994) 1309.

Rohlin, J.H. and Lodding, A. *Z.Naturfosch.* **17A** (1962) 1081.

Rothman, S.J. and.Hall, L.D. *Trans.A.I.M.E.* **206** (1956) 199.

Rucknestein, E.and Liu, H. *Ind.Eng.Chem.Res.* **36** (1997) 3927.

S.Chapman, S. and Cowling, T.G. *The Mathematic Theory of Non-uniform Gases.* Cambridge University Press, New York, 1970.

Sengupta, R., Bhattacharya, R. and Guna, A. *Ind.J.pure&App.Phys.* **15** (1977) 164.

Smithells, C.J. *Metal Reference Book* (3rd edition), Butter Worths, Washington, D.C, 1962.

Spells, K.E. *Proc.Phys.Soc* .**48** (1936) 299.

Swallin, R.A. *Acta.Metall.* **7** (1959) 736.

Tyrrel, H.J.V. *Sci.Prog.* **67** (1981) 271.

Vadovic, C.J. and Colver, C.P. *Phys.Rev.B.* **1** (1970) 4850.

Verlet, L. *Phys.Rev.* **159** (1967) 98.

Walsdorfer, H. *Z.Met.* **79** (1983) 654.

Wills, J.M., and Harrison, W.A. *Phys.Rev.* **28B** (1983) 4363.

Yang, L., Simnad, M.T. and Derge, G. *Trans.A.I.M.E.* **206** (1956) 1577.

Yao, T.P. and Kondic, V. *J.Inst.Met.* **81** (1952 –53) 17.

Zhen, S. and Davies, G.J. *Phys.Stat.Sol.* **78A** (1983) 595.

Zwanzig, R. and Harrison, A.K. *J.Chem.Phys.* **83** (1985) 5861
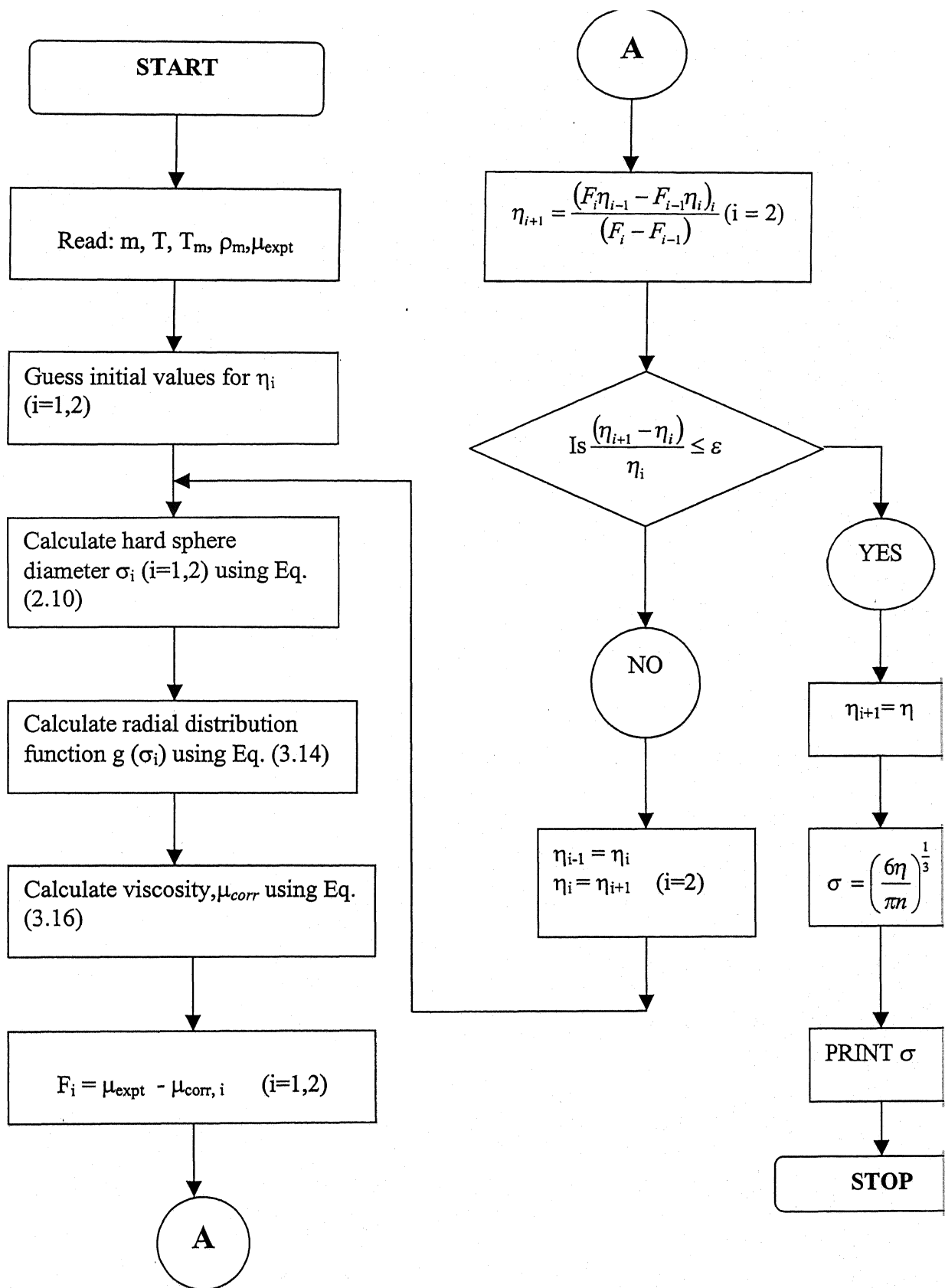
APPENDIX A

Fig A: Flow chart for the calculation of hard sphere diameter from experimental viscosity data.

APPENDIX B

Table B Liquid metals and their physical properties.

S.No	Metal	M	T_m (K)	ρ_m (10^3 kg/m³)	$-\Lambda$ (10^{-1} kg/m³ K)
1	Ag	107.87	1233.65	9.33	9.10
2	Bi	208.9	544.1	10.05	11.8
3	Cd	112.24	594	8.01	12.2
4	Cs	132.9	301.65	1.84	5.70
5	Cu	63.54	1356	8.00	8.01
6	Ga	69.72	303	6.10	5.60
7	Hg	200.5	234.28	13.69	24.2
8	In	114.82	429.55	7.03	6.80
9	K	39.09	336.75	0.83	2.40
10	Li	6.94	452	0.518	1.00
11	Na	22.98	371.05	0.927	2.35
12	Pb	207.2	600.55	10.67	13.2
13	Rb	85.5	311	1.48	4.50
14	Sn	118.6	505	6.98	6.10
15	Tl	204.3	576	11.35	13.0
16	Zn	65.38	692.6	6.58	9.80